



Survey and Down-Selection of Acid Gas Removal Systems for the Thermochemical Conversion of Biomass to Ethanol with a Detailed Analysis of an MDEA System

**Task 1: Acid Gas Removal Technology
Survey and Screening for
Thermochemical Ethanol Synthesis**

March 2009

**Task 2: Detailed MDEA Process
Analysis**

September 2009

*Nexant Inc.
San Francisco, California*

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency & Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

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NREL Technical Monitor: Andy Aden

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Task 1
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Prepared for:
United States Department of Energy / National Renewable Energy
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Contents

Section	Page
Executive Summary	1
Section 1 Introduction	5
Section 2 Study Approach	7
Section 3 Chemical Absorption Processes	13
Section 4 Physical Absorption Processes	22
Section 5 Hybrid Processes	29
Section 6 Hot Carbonate-Based Process	32
Section 7 RTI Solid Absorbent-Based Process	37
Section 8 Liquid Phase Oxidation Processes	41
Section 9 Membrane Separation Processes	44
Section 10 Conclusions and Recommendations	47
References	49

Figures

Figure ES-1 Order-of-Magnitude Comparison of CO and Hydrocarbons Absorption in a Selexol and MDEA Process	3
Figure 1-1 Overview of NREL Thermochemical Ethanol Synthesis Process	5
Figure 2-1 Gas Cleanup and Conditioning Process of NREL Alcohol Synthesis Design	8
Figure 2-2 Process Selection Chart for Simultaneous H ₂ S and CO ₂ Removal	11
Figure 2-3 Process Selection Chart for H ₂ S Removal	12
Figure 2-4 Process Selection Chart for CO ₂ Removal	12
Figure 3-1 Typical Amine Process Flow Diagram	17
Figure 4-1 Typical Selexol Process Flow Diagram	24
Figure 4-2 Typical Selective Selexol Process Flow Scheme	25
Figure 4-3 Order-of-Magnitude Comparison of CO and Hydrocarbons Absorption in a Selexol and MDEA Process	27
Figure 5-1 Typical Sulfinol Process Flow Diagram	30
Figure 6-1 Typical Hot Potassium Carbonate Single-Stage Process	33
Figure 6-2 Typical Hot Potassium Carbonate Split-Flow Process	34
Figure 6-3 Typical Hot Potassium Carbonate Two-Stage Process	34
Figure 7-1 Simplified Overall WGPU Process Scheme	39
Figure 7-2 High Temperature Desulfurization (HTDS) Process Flow Scheme	39
Figure 8-1 Conventional LO-CAT System	42
Figure 9-1 One-Stage Membrane System	45
Figure 9-2 Two-Stage Membrane System	46

Tables

Table ES-1	Cost Components of the Gas Cleanup and Conditioning Process Area	1
Table 2-1	Design Basis for AGR Process Screening.....	8
Table 3-1	Chemical Absorption Processes Summary Table.....	19
Table 3-2	Estimated Amine Circulation Rates and Regeneration Energy for NREL Design.....	21
Table 4-1	Selexol Solvent Relative Solubility of Gases	24
Table 4-2	Physical Absorption Processes Summary Table	28
Table 5-1	Hybrid Processes Summary Table	31
Table 6-1	Hot Potassium Carbonate Processes Summary Table.....	36
Table 8-1	Liquid Phase Oxidation Processes Summary Table.....	43

Acronyms

AGR	acid gas removal
BFW	boiler feed water
DEA	diethanolamine
DGA	diglycolamine
DIPA	diisopropanolamine
DSRP	direct sulfur recovery process
HCs	hydrocarbons
HTDS	high temperature desulfurization
IGCC	integrated gasification combined cycle
MDEA	methyldiethanolamine
MEA	monoethanolamine
MM	million (1×10^6)
MW	molecular weight
NREL	National Renewable Energy Laboratory
O&M	operating and maintenance
ppm	parts per million
ppmv	parts per million volume
RTI	Research Triangle Institute
SCF	standard cubic feet (1 atm, 60°F)
TIC	total installed cost
UOP	Universal Oil Products
WGPU	warm gas clean up

Executive Summary

NREL's recent published report, "Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass" (NREL/TP-510-41168), evaluated the techno-economics of a biomass gasification process to produce synthesis gas (syngas) for ethanol synthesis. The thermochemical ethanol production process consists of five major process areas: feed handling and preparation, gasification, gas cleanup and conditioning, alcohol synthesis, and product separation. The report showed that the syngas cleanup and conditioning section, which consists of tar reforming and catalyst regeneration, syngas cooling and compression, and acid gas removal (AGR) operations, has the highest cost component of all the process areas, accounting for approximately 39% of the total installed plant cost (Table ES-1). As such, this process section has a significant impact on the overall thermochemical ethanol production economics. In NREL's current design, acid gas removal is performed by an MEA system (a chemical absorption process). NREL wishes to examine the applicability of other acid gas removal processes (e.g. physical absorption systems of Selexol and Rectisol) to the thermochemical ethanol synthesis design, and to develop a detailed acid gas removal process design in order to better assess its technical and economic impacts on the overall process.

Table ES-1 Cost Components of the Gas Cleanup and Conditioning Process Area

Units of the gas clean up conditioning process	Cost, as % of TIC
Tar Reforming and Catalyst Regeneration	13.4
SynGas Cooling	3.4
SynGas Compression	12.9
AGR	8.9
Total	38.6

Objectives of the current study are to conduct a survey and screening of various acid gas removal processes in order to evaluate their capability to meet the specific design requirements provided by NREL, and to recommend applicable acid gas removal options for a more detailed analysis in Task 2. In NREL's design, the raw syngas enters the AGR unit at 420 psia, and contains 234 ppmv H₂S, 11 mol% CO₂, and trace amounts of hydrocarbon impurities. The required purity of the treated gas for alcohol synthesis is 50 ppmv H₂S and 5.1 mol% CO₂. This corresponds to 79% removal of H₂S and 59% removal of CO₂.

The capability and applicability of the various acid gas removal processes are qualitatively evaluated based on the following criteria:

- Feed gas compositions and conditions
- The desired purity of the treated gas
- Compatibility of process solvent with impurities in the feed gas
- Selectivity of H₂S over CO₂
- Commercial experience of the AGR processes with synthesis gases
- Relative costs of the AGR processes.

The acid gas removal requirements for the NREL ethanol synthesis design can be met by a number of chemical and physical absorption processes. The final selection would most likely be based on considerations of plant costs (capital and O&M), commercial experience, and process reliability and operational flexibility. Other important factors that influence the design and selection of an AGR system must also be considered, including:

- Syngas compression before AGR – Since syngas compression accounts for 13% of the total biomass-to-ethanol plant cost, the AGR unit should operate at the lowest possible pressure to minimize the power and equipment cost penalties associated with the compression of the syngas up to the operating pressure of the AGR unit. For this study, all AGR options are qualitatively evaluated at the fixed operating pressure of 420 psia, which eliminates the need to consider the syngas compression differences. In the NREL design, the alcohol synthesis is carried out at 990 psia. Therefore, the operating pressure range in which the AGR unit can theoretically be operated would be from the tar reformer pressure of 15 psia up to the alcohol synthesis pressure of 990 psia. For AGR processes that favor high operating pressures, the detailed analysis in Task 2 requires a trade-off analysis to assess the power and cost penalties associated with the additional compression.
- Absorption of product gases – The AGR feed gas contains a high concentration of CO and small quantities of hydrocarbons, ranging from methane to pentane, benzene and tar, which would be absorbed to some extent into the treating solutions. Absorption of CO and hydrocarbons is expected to be greater for physical absorption than chemical absorption systems due to the higher solubility of these compounds in a physical solvent. The loss of CO through absorption, if significant, would negatively affect the yield of the alcohol synthesis process and the overall plant efficiency.

Equally important, the absorption of CO and hydrocarbon gases into the treating solvents has an environmental impact on the overall process since these gases, which exit the AGR unit with the acid gas stream, would be vented with the CO₂ stream from the LO-CAT sulfur recovery unit (Figure 1-1, Section 1). The incineration of the CO₂ vent gas to destroy the CO and hydrocarbons would consume a significant amount of product gas as fuel as well as increase the overall plant cost.

The concentrations of CO (a criteria pollutant) and hydrocarbons (greenhouse gases) in the CO₂ vent stream can be minimized by depressuring the rich solution and recycling the flashed gas to the absorber. The flash pressure can, however, influence the level of contaminant in the CO₂ vent gas. At low flash pressures, less CO and hydrocarbons will be present in the CO₂ vented stream, but the cost for recycling the flashed offgas to the absorber would increase and can negatively impact the overall process economics. In comparison to a chemical absorption system, a physical solvent system is expected to have higher concentrations of CO and hydrocarbons in the vented stream. Preliminary process simulation of this effect was performed and the results are shown in Figure ES-

1. The allowable CO and hydrocarbons concentrations in the CO₂ vent stream are site-specific and need to be established prior to the start of Task 2 detailed analysis.

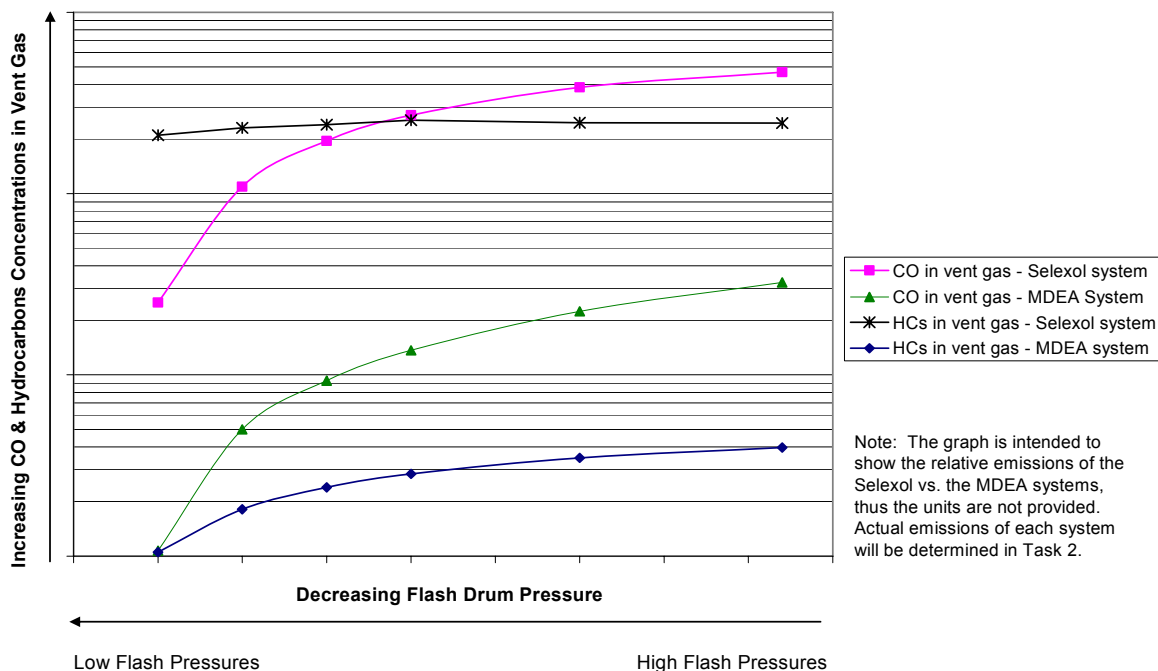


Figure ES-1 Order-of-Magnitude Comparison of CO and Hydrocarbons Absorption in a Selexol and MDEA Process

- Selective removal of H₂S vs. CO₂ – The alcohol synthesis catalyst requires an H₂S concentration of up to 50 ppmv to maintain catalyst activity, and it can also tolerate a CO₂ concentration of up to 5 mol%. The type of AGR solvents used will affect the degree of H₂S and CO₂ removal. Primary and secondary amines are known for their non-selectivity, and can remove comparatively more CO₂ than H₂S from the feed syngas stream. To meet the 50 ppmv H₂S specification in the treated clean syngas, excess amount of CO₂ would probably also be removed, yielding a gas with a much lower CO₂ content than 5 mole%. The exact CO₂ vs. H₂S content in the cleaned gas would need to be confirmed by process simulation.

In comparison, a tertiary amine process such as MDEA and physical solvent systems of Selexol and Rectisol can selectively remove first H₂S then CO₂ from a feed gas stream, and thus in principal, has a higher degree of control with meeting the needed clean syngas specification. Also, MDEA has a lower circulation rate and regeneration energy requirement than primary and secondary amine processes of MEA and DEA respectively.

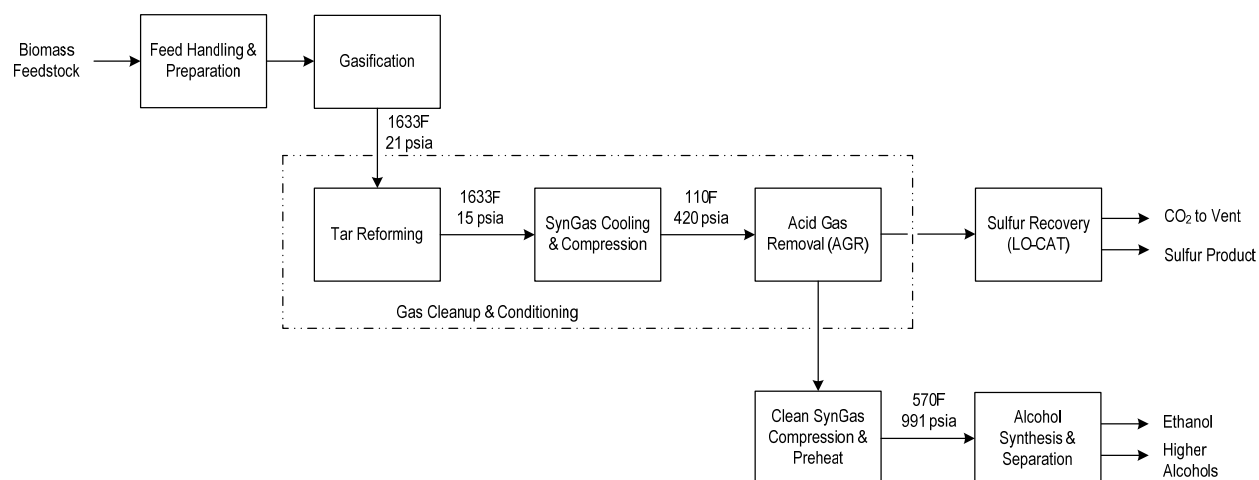
A qualitative assessment, taking into consideration the factors mentioned above and the process screening criteria cited in the report, suggests that MDEA and Selexol are both viable AGR options for the thermochemical ethanol synthesis application to warrant of a more detailed design/system analysis study. The Selexol process is recommended over Rectisol, because, in general, it has a lower cost. The Rectisol process is generally known for its demonstrated ability to provide stringent purity syngas for applications such as coal-to-chemicals, synthetic natural gas, and Fischer-Tropsch liquids production. It can achieve complete removal of sulfur (i.e., <0.1 ppm H₂S plus COS) as well as removal of HCN, NH₃ and trace metal carbonyls, which can be poisonous to synthesis catalysts. Thus, unless there are trace contaminants in the raw gas that have not yet been identified and that can potentially damage the ethanol synthesis catalyst, a more costly Rectisol unit would not be justified for the NREL design.

Limited analysis, based on in-house cost and design data available, suggests that while, in general, a Selexol process would have a higher plant cost than a MDEA process at the given operating conditions and acid gas partial pressures, it may become more economical as the system pressure increases. The effect must be evaluated against the cost of syngas compression and the impact of increased product gas absorption at high pressures with the use of the Selexol system.

A detailed process design and cost estimation analysis of the MDEA system for thermochemical ethanol production is recommended, as Task 2 activity. In addition, a comparative study for the Selexol system, taking into consideration the various plant design parameters such as the overall syngas compression cost and the environmental impact of CO and hydrocarbons emissions requirement, etc., is also recommended.

1.1 BACKGROUND

For alcohol synthesis processes, the removal of acid gas compounds is an important process to prepare the syngas to achieve the required purity in order to avoid poisoning and deactivation of the synthesis catalyst. Acid gas generally includes H_2S , CO_2 , HCN , and organic sulfur compound such as COS , CS_2 , and mercaptans. Figure 1-1 illustrates a simplified block flow diagram of the NREL thermochemical ethanol synthesis design. The feed gas to the AGR unit is relatively clean, with CO_2 and H_2S being the primary acid gas compounds. In the current design, an MEA system is used for the removal of acid gases from the syngas stream. A LO-CAT unit is used for sulfur recovery.



Source: Reference [1]

Figure 1-1 Overview of NREL Thermochemical Ethanol Synthesis Process

1.2 OBJECTIVES

The objectives of this study, Task 1, are to conduct a survey and screening of various acid gas removal processes in order to evaluate their capability to meet the specific design requirements provided by NREL for thermochemical ethanol production, and to recommend suitable acid gas removal options for the detailed analysis in Task 2. As agreed with NREL, the following types of acid gas removal processes are to be surveyed and screened:

1. Chemical absorption (used in current NREL design)
2. Physical absorption
3. Hybrid processes

4. Hot carbonate-based processes
5. RTI solid absorbent-based process
6. Liquid phase oxidation
7. Membrane separation

The qualitative process screening performed to select the applicable acid gas removal processes for the NREL alcohol synthesis design is based on the design basis provided by NREL, the screening criteria outlined in the Methodology Section, and the performance data of the AGR process developed from the survey.

This study begins with a survey of various types of acid gas removal process, followed by a qualitative screening to determine the applicability of each process for thermochemical ethanol synthesis. The following sections discuss the types of acid gas removal technologies included in the survey, and the design basis and the screening criteria used for the qualitative process screening.

2.1 ACID GAS REMOVAL TECHNOLOGIES SURVEYED

This study conducts a survey of the following acid gas removal technologies. The survey includes an overview and performance of each process and discusses the process advantages and disadvantages as compared to the chemical absorption process.

1. Chemical absorption (used in current NREL design)
2. Physical absorption
3. Hybrid processes
4. Hot carbonate-based processes
5. RTI solid absorbent-based process
6. Liquid phase oxidation
7. Membrane separation

2.2 QUALITATIVE PROCESS SCREENING OF ACID GAS REMOVAL PROCESSES

A qualitative process screening is performed to assess the suitability of the acid gas removal processes for the NREL thermochemical ethanol synthesis design, using the design basis and screening criteria below.

2.2.1 Design Basis

Figure 2-1 illustrates a simplified block flow diagram of the syngas cleanup and conditioning process in the NREL thermochemical ethanol production design. The feed gas to the AGR and the treated gas specifications are provided by NREL and are used as basis for the qualitative process screening. The design basis is shown in Table 2-1.

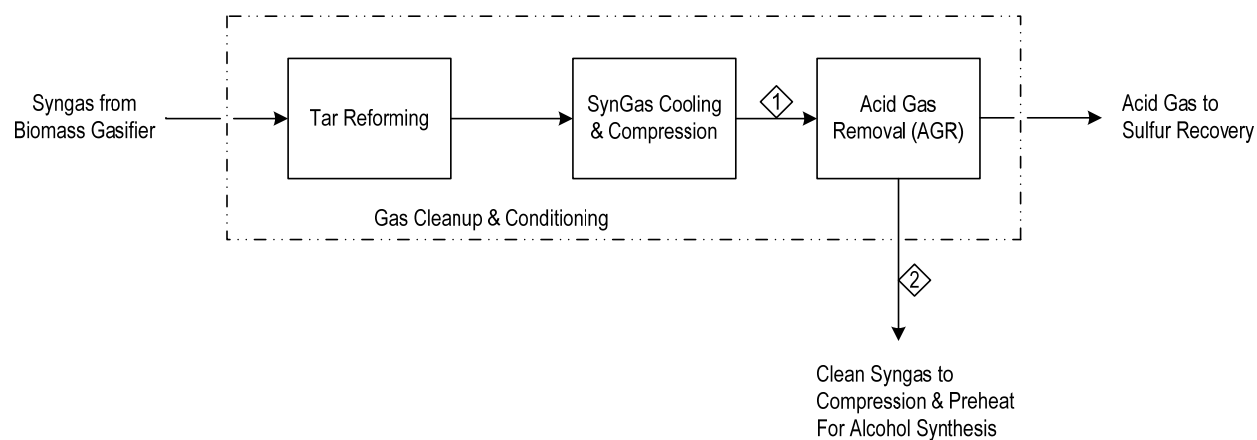


Figure 2-1 Gas Cleanup and Conditioning Process of NREL Alcohol Synthesis Design

Table 2-1 Design Basis for AGR Process Screening

Stream No.	1 Feed Gas to AGR	2 Treated Gas
Total Flow, lbmol/hr	17,942	16,740
Temperature, °F	110	110
Pressure, psia	420	415
Vapor Fraction	1	1
Compositions	mole%	mole%
H ₂	42.9	45.9
H ₂ O	0.3	0.3
CO	42.9	46.0
N ₂	0.8	0.9
CO ₂	11.4	5.1
H ₂ S	234 ppmv	50 ppmv
NH ₃	82 ppmv	88 ppmv
Methane (CH ₄)	1.4	1.5
n-Butane (C ₄ H ₁₀)	0.03	0.03
Ethane (C ₂ H ₆)	13 ppmv	14 ppmv
Ethylene (C ₂ H ₄)	0.1	0.1
Acetylene (C ₂ H ₂)	0.0	0.0
Propane (C ₃ H ₈)	0.2	0.2
Pentane +	42 ppmv	46 ppmv
Benzene (C ₆ H ₆)	3 ppmv	3 ppmv
Tar (C ₁₀ H ₈)	0.4 ppmv	0.5 ppmv

Source: Reference [1]

2.2.2 Process Screening Criteria

The qualitative process screening assesses the following criteria for applicability and overall consideration with selecting an AGR process for the NREL thermochemical ethanol synthesis design:

- Feed gas compositions and conditions – The feed gas conditions and partial pressure of acid gas components influence the performance and selection of AGR process. Numerous graphs have been published showing the approximate guidelines for the selection of various solvent-based processes based on the acid gas partial pressure in the feed gas and in the treated gas^[14]. Figure 2-2 shows a general guideline that can be used to select an appropriate process for a feed stream that contains both CO₂ and H₂S. Similar general selection guidelines for removal of only H₂S or CO₂ are shown in Figures 2-3 and 2-4 respectively. Selection process depends on the acid gas partial pressure in the feed against the desired acid gas concentration in the treated gas.
- The required purity of the treated gas – The required clean gas specifications usually depend on its end use. In the NREL thermochemical ethanol production process, the alcohol synthesis catalyst requires an H₂S concentration of up to 100 ppm (50 ppmv) to maintain catalyst activity, and it can also tolerate a CO₂ concentration of up to 5 mol%. According to NREL, the CO₂ concentration in the clean gas can range from 1 to 5 mol%. On this basis, the acid gas removal process is not required to achieve deep H₂S and CO₂ removal. Based on the feed gas compositions and the treated gas specifications, the required acid gas removal is 79% of H₂S and 59% of CO₂.
- Chemical compatibility – The primary concern with chemical compatibility is the irreversible reactions of the solvent with impurities such as HCN or organic sulfur compounds (COS, CS₂, and mercaptans), which result in solvent degradation and solvent losses. As shown in the design basis, the impurities in the feed gas to the AGR unit in the NREL design consist of mostly CO₂ and H₂S, a small amount of ammonia, and essentially no organic sulfur compounds. Thus, chemical incompatibility of the treating solvent with impurities in the feed gas is unlikely to be a concern for the current design.

However, if experimental data show that the biomass-derived syngas does indeed contain any of these impurities (HCN, COS, CS₂, or mercaptans), then MEA may not be a suitable solvent due to the irreversible reactions of MEA with COS and CS₂. All other amine solutions (DEA, DGA, DIPA, and MDEA) and physical solvents evaluated in this study are able to tolerate such impurities.

- Selectivity of H₂S over CO₂ – In the NREL's design, although some level of sulfur removal is required to meet the specifications for alcohol synthesis, the bulk of the acid gas removal is CO₂. Primary and secondary amines are known for their non-selectivity, and can remove comparatively more CO₂ than H₂S from the feed syngas stream. To meet the 50 ppmv H₂S specification in the treated clean syngas, excess amount of CO₂

would probably also be removed, yielding a gas with a much lower CO₂ content than 5 mole%. The exact CO₂ vs. H₂S content in the cleaned gas would need to be confirmed by process simulation.

In comparison, a tertiary amine process such as MDEA and physical solvent systems of Selexol and Rectisol can selectively remove first H₂S then CO₂ from a feed gas stream, and thus in principal, has a higher degree of control with meeting the needed clean syngas specification. Also, MDEA has a lower circulation rate and regeneration requirement than primary and secondary amine process of MEA and DEA respectively.

- Absorption of product gases – The NREL AGR feed gas contains a high concentration of CO and small quantities of hydrocarbons, ranging from methane to pentane, benzene and tar, which would be absorbed to some extent into the treating solutions. Absorption of CO and hydrocarbons is expected to be greater for physical absorption than chemical absorption systems due to the higher solubility of these compounds in a physical solvent. The loss of CO through absorption, if significant, would negatively affect the yield of the alcohol synthesis process and the overall plant efficiency. Additionally, the absorption of CO and hydrocarbon gases into the treating solvents has an environmental impact on the overall process since these gases would be vented with the CO₂ stream from the LO-CAT sulfur recovery unit.
- Syngas compression before AGR – Since syngas compression accounts for 13% of the total biomass-to-ethanol plant cost, the AGR unit should operate at the lowest possible pressure to minimize the power and equipment cost penalties associated compression of the syngas up to the operating pressure of the AGR unit. For this study, all AGR options are qualitatively evaluated at the fixed operating pressure of 420 psia, which eliminates the need to consider the syngas compression differences. In the NREL design, the alcohol synthesis is carried out at 990 psia. Therefore, the operating pressure range in which the AGR unit can theoretically be operated would be from the tar reformer pressure of 15 psia up to the alcohol synthesis pressure of 990 psia. For AGR processes that favor high operating pressures, the detailed analysis in Task 2 requires a trade-off analysis to assess the power and cost penalties associated with the additional compression.
- Commercial experience – The various acid gas removal processes surveyed in this study, with the exception of RTI's Warm Gas Clean Up process, are commercially available. Selected chemical and physical absorption processes have been commercially demonstrated with coal-derived gases. Since the raw gas in the NREL thermochemical ethanol production is relatively clean in comparison to a typical syngas from coal gasification, its treatment should be relatively easier. Thus, commercially demonstrated acid gas removal processes for coal-gasification derived gases are a good starting point for the preliminary screening exercise.
- Relative costs of processes – The acid gas removal requirement for the NREL ethanol synthesis can be met by a number of chemical and physical absorption processes. The

final selection ultimately depends on economics of the integrated process, and not just of the AGR process by itself. The integration effects of the AGR system on the overall thermochemical ethanol production process also need to be considered.

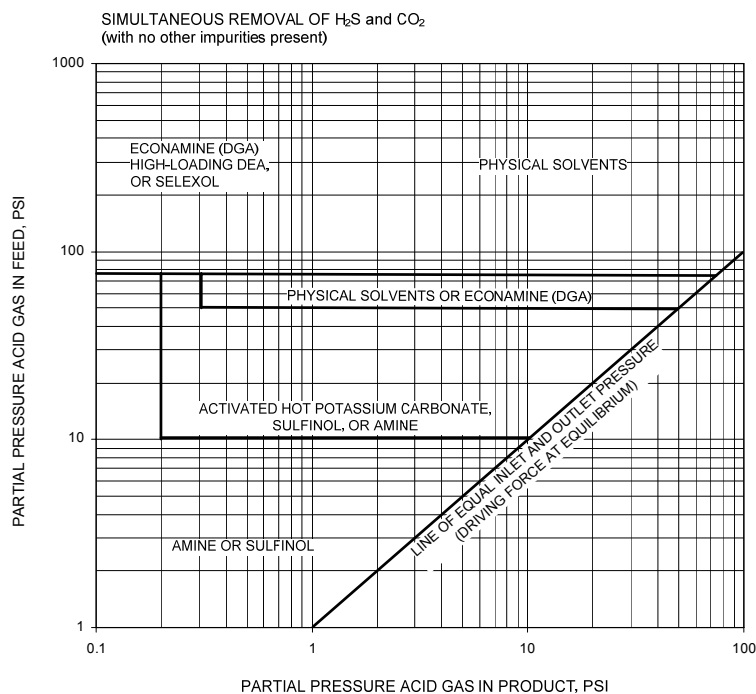


Figure 2-2 Process Selection Chart for Simultaneous H₂S and CO₂ Removal

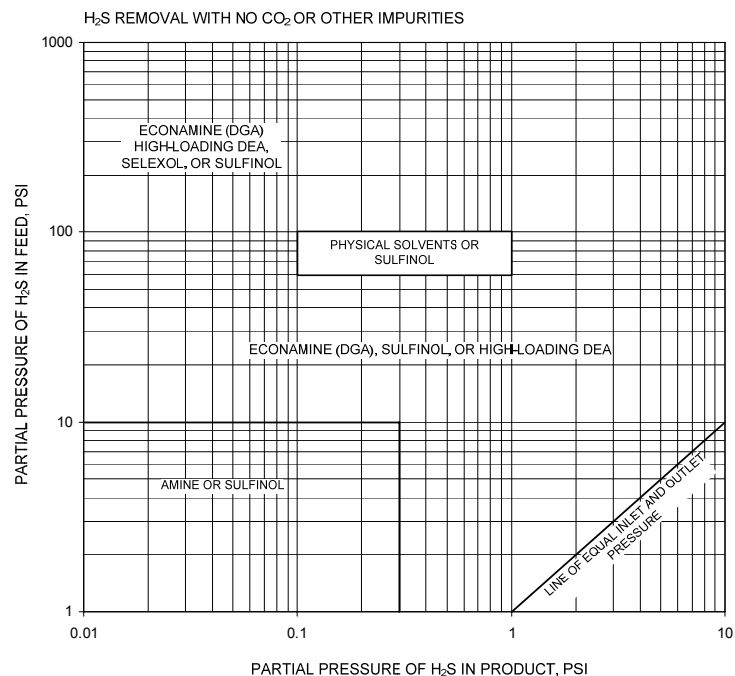


Figure 2-3 Process Selection Chart for H₂S Removal

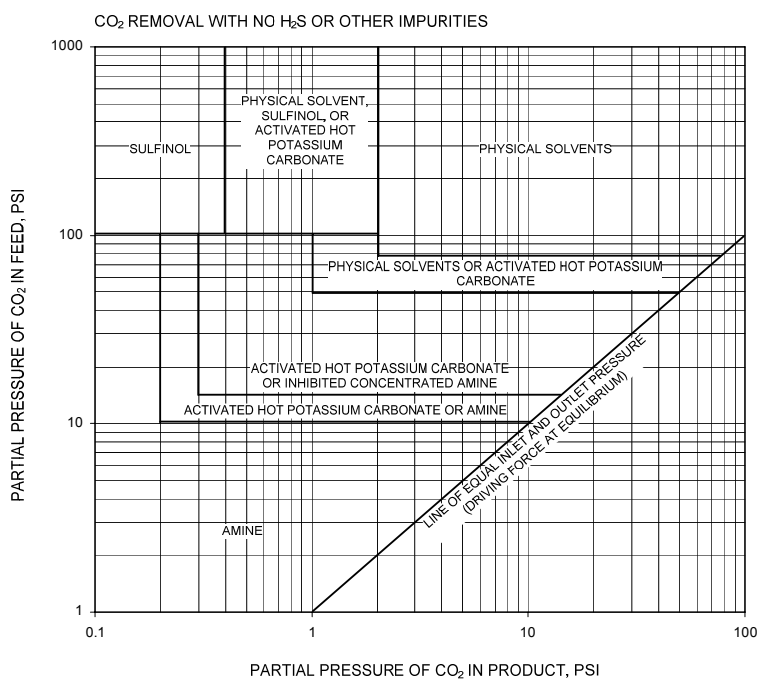


Figure 2-4 Process Selection Chart for CO₂ Removal

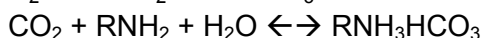
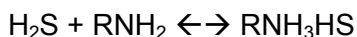
Source: reference [14]

An overview of the chemical absorption process is presented in this section. The process characteristics and operating parameters are provided in a summary table at the end of the section.

3.1 PROCESS OVERVIEW

In a chemical absorption process, the acid gas components react with the solvent to form a chemical compound. The solvent can be regenerated by the application of heat to strip the absorbed gases. Typical of chemical absorption is the amine process. Amines are commonly used in the petroleum refining and natural gas processing industries for acid gas removal. Additionally, amine (e.g. MDEA) has also been used to treat synthesis gas from coal gasification.

The three basic types of amines that are available commercially include: primary amine, such as MEA or DGA, secondary amine, such as DEA or DIPA, and tertiary amines, such as MDEA. Primary and secondary amines react with H₂S and CO₂ as follows:



where R represents the hydrocarbon and the hydroxyl groups in amine solution

The reactions proceed to the right at increased acid gas partial pressures and/or low temperatures and are reversed at low partial pressures and/or high temperatures. In most primary and secondary amine solutions, H₂S and CO₂ react simultaneously with the solution, making selective recovery difficult. Primary and secondary amines react with CO₂ to form carbamate. Carbamate formation limits the solution loading capacity for CO₂ to approximately 0.5 mole of CO₂ per mole of amine. Tertiary amines, however, cannot react directly with CO₂ to form carbamate. In tertiary amine solutions, the reaction with CO₂ forms bicarbonate, and the CO₂ reaction rate is significantly slower than that of H₂S with tertiary amines; therefore, tertiary amines generally exhibit greater selectivity for H₂S in the presence of CO₂.

The removal of organic sulfur compounds (COS and CS₂) is generally accomplished by the hydrolysis unit upstream of the amine unit. The hydrolysis unit converts the COS and CS₂ into H₂S, which can then be removed by the amine unit. COS and CS₂ can be partially removed by some amines, especially primary and secondary ones. However, removal of such gas impurities subject the solution to degradation as those impurities react, either reversibly or irreversibly, with the amines to form degradation products. In irreversible reactions, such as those of MEA with COS and CS₂, formation of nonregenerable degradation products result in excessive solvent losses if the gas contains high concentrations of those sulfur compounds. After prolonged use, accumulation of the degradation products in the solution reduces its absorption efficiency. These contaminants are commonly removed from the solution by thermal reclaiming.

In addition to the basic amines, proprietary amines are also offered by many chemical companies, such as UOP (Amine Guard and UCARSOL), BASF (Activated MDEA), or Shell (ADIP-X). Proprietary formulations, usually consisting of mixtures of amines and additives, are used to meet specific gas treating targets such as selective H₂S removal, partial or complete CO₂ removal, high acid gas loading, COS removal^[2], etc.

The selection of an amine solution depends on process conditions, acid gas partial pressures, and purity of the treated gas. Generally, amine processes are suitable for applications with low to medium acid gas partial pressures as the process economic advantage declines with increasing partial pressures of acid gases. The economy of an amine process is largely determined by the solvent regeneration energy requirements, which is a function of the heats of reaction of H₂S and CO₂, and the solution circulation rate, which is based on the solution capacity and concentration. Increasing the solution concentration can generally reduce the circulation rate, thereby reducing the plant cost; however, in order to avoid equipment corrosion, the solution concentration should not exceed the upper limit recommended for the solvent type.

A comparison of the basic amines is provided below. Table 3-1 summarizes the characteristics and performance of the various amines.

Monoethanolamine (MEA)

MEA is generally used in natural gas processing plants to treat gases containing only H₂S and CO₂ in low concentrations, especially when maximum removal of both impurities is required. MEA solutions have the following advantages:

- High alkalinity, which increases the solution effectiveness for acid gas absorption
- High solution capacity at moderate concentrations
- Contaminated solutions can be reclaimed with relative ease

The MEA process also has a number of disadvantages, including:

- The formation of irreversible reaction products with COS and CS₂, which leads to excessive solution losses when the raw gas contains high concentrations of those impurities^[2]
- Higher corrosion rates compared to other amines, especially if the MEA concentration exceeds 20% and the solution acid gas loading is high^[2]
- High heat of reaction with CO₂ and H₂S, resulting in high energy requirements for solvent regeneration
- A relatively high vapor pressure, resulting in high vaporization losses in low-pressure operations

Diethanolamine (DEA)

DEA has been used for many years to treat refinery gases which often contain COS and CS₂ in addition to CO₂ and H₂S. The advantages and disadvantages of DEA as compared to MEA are as followed:

- The acid gas loading is typically higher for DEA than MEA (see Table 3-1)^[5]
- DEA forms regenerable compounds with COS and CS₂, thus, partial removal of COS and CS₂ can be achieved without significant solution degradation^[2]
- Requires lower energy for solvent regeneration than MEA due to lower heats of reaction
- Low solvent vapor pressure makes DEA suitable for low-pressure operations
- The reclaiming of contaminated solutions is more complex since vacuum distillation may be required^[2]

Diglycolamine (DGA)

DGA has been used for the treatment of both natural and refinery gases due to its capability to remove not only H₂S and CO₂, but also COS and mercaptans. The DGA process is similar to that of the MEA process in many respects, except that the low vapor pressure of DGA allows its use in relatively high concentrations (40-60 wt%), which results in lower circulation rates and steam consumption.

Diisopropanolamine (DIPA)

DIPA has been used primarily in Europe for the treatment of refinery gases and liquids that contain COS in addition to H₂S and CO₂. DIPA solutions are reported to have low steam consumption, to be noncorrosive, and to be capable of removing considerable amounts of COS without causing solution degradation^[2]. Additionally, DIPA also exhibits some selectivity for H₂S over CO₂, although H₂S selectivity is not as great as that of tertiary amines. Because of its H₂S selectivity, DIPA has been used for Claus plant tail gas treating.

Methyldiethanolamine (MDEA)

MDEA selectively removes H₂S while allowing a large fraction of CO₂ to slip through unabsorbed. MDEA has been used for selective H₂S removal in various applications, including natural gas processing, Claus tail gas treating, and synthesis gas treating for integrated gasification combined cycle (IGCC) process. MDEA offers a number of advantages, including:

- Selective removal results in a reduction of the amount of acid gas removed, thus, compared to other amine systems, MDEA system is more economical with respect to solvent circulation rates and energy requirements^[2]
- Low heats of reaction result in low regeneration energy
- MDEA's low corrosion rates—the least corrosive of the amines—and its low vapor pressure permit its use in high concentrations (up to 60 wt%), which results in lower circulation rates, and thereby, smaller plant size and lower plant costs^[2]
- MDEA has high solution capacity, and excellent thermal and chemical stability

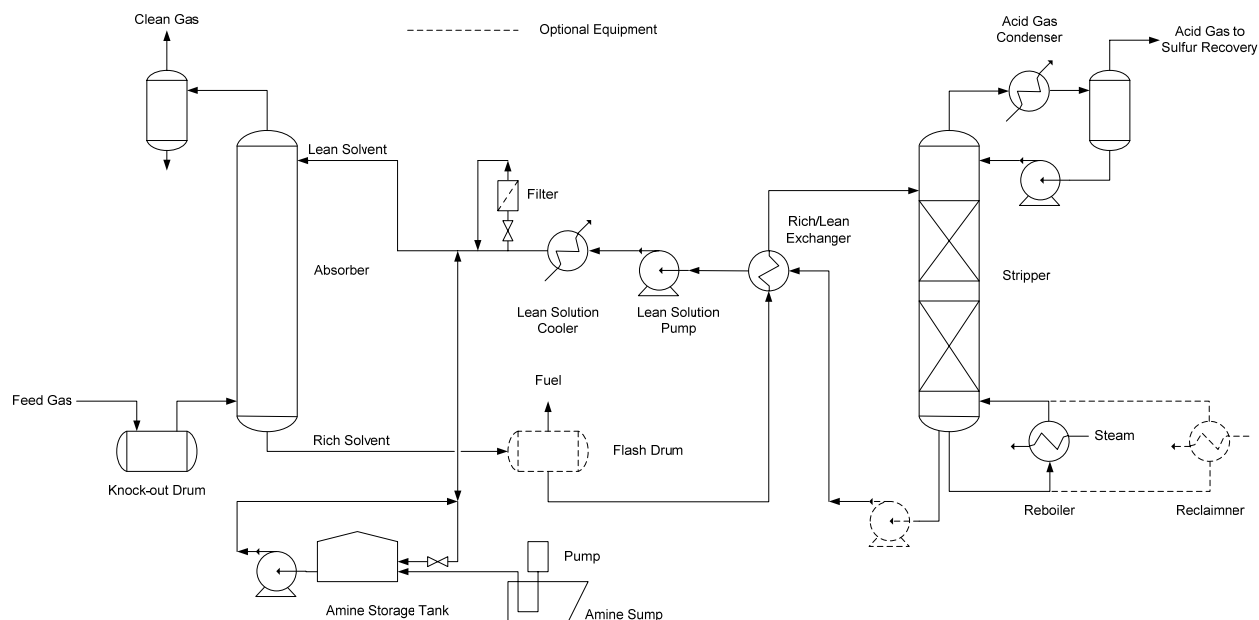
- MDEA is only sparingly miscible with hydrocarbons, which is an advantage over physical absorption processes (discussed in Section 4) when treating gases rich in hydrocarbons since hydrocarbon losses can be minimized

Due to the many favorable attributes of MDEA, its use as a nonselective solvent for the removal of high concentrations of CO₂ is of considerable interest. In order to enhance MDEA's capability for CO₂ removal, proprietary additives are added in various proportions to the MDEA solution to achieve the desired removal target. The formulation of these propriety amines can be designed from high H₂S/CO₂ selectivity to complete H₂S and CO₂ removal.

3.1.1 Flow Scheme

Figure 3-1 illustrates a typical amine process. The feed gas enters a knock-out drum to remove any condensate. The dry feed gas then enters at the bottom of the absorber and is contacted countercurrently with the lean amine solution flowing down from the top. As the solution contacts the gas stream, the acid gases react with the amine. The sweet gas stream exits at the top of the absorber. The rich amine solution from the bottom of the absorber enters a flash drum where any dissolved hydrocarbons are removed. The recovered hydrocarbons are generally used as plant fuel. The rich amine solution is heated by heat exchange with the lean solvent stream and enters the stripper where the acid gases are stripped from the solution as it flows down the column to the reboiler. The lean solution exits the stripper, exchanges heat with the rich solution stream, and is further cooled before it enters at the top of the absorber. The stripped acid gas stream is cooled to recover water and is then sent to a sulfur recovery unit for processing.

An important design consideration for amine processes is corrosion. In water, H₂S dissociates to form a weak acid while CO₂ forms carbonic acid. These acids attack and corrode metal. Therefore, process equipment that is exposed to CO₂/H₂S evolution (i.e. stripper overhead) is normally clad with stainless steel.



Source: Adapted from reference [5]

Figure 3-1 Typical Amine Process Flow Diagram

3.2 PROCESS APPLICABILITY TO THERMOCHEMICAL ETHANOL SYNTHESIS

Table 3-1 provides a performance summary of the various amine processes surveyed. The applicability of these amine processes to the NREL ethanol synthesis design is qualitatively screened and assessed, based on the syngas design basis and criteria outlined in Section 2.

In NREL's current design, the AGR feed gas has an H_2S partial pressure of 0.1 psia and a CO_2 partial pressure of 48 psia. The treated gas has an H_2S partial pressure of 0.02 psia and a CO_2 partial pressure of 21 psia. The acid gas partial pressure is high enough that a number of AGR processes can be applicable. General selection guideline of Figure 2-2 shows that amine processes, along with hot potassium carbonate and physical solvent systems, can potentially be used for the NREL design.

Amine solvents – In general, primary and secondary amines are more reactive (i.e., form stronger bond with) than tertiary amines to acid gases and hence more cost effective at low pressures, whereas MDEA being less reactive, is more competitive at high pressures. The NREL design feed gas is at sufficiently high pressure such that the MDEA process should be given a serious design consideration, given its known advantages:

- Less corrosive,
- More resistant to irreversible degradation by impurities as such COS and CS_2 normally presence in syngas, of which NREL syngas doesn't seem to contain them,

- Lower heat of regeneration,
- Relatively lower vapor pressure loss,
- Can be designed to selectively remove H₂S and CO₂, if needed.

Both MEA and MDEA are widely used in the natural gas and refinery industries, and the processes are amenable to analysis via several commercial process simulators. Commercial licensed processes normally contain proprietary additives to control degradation and/or augment the solvents' absorption rate.

Preliminary PROMAX simulation using NREL design syngas - Process modeling indicates that the CO₂ content in the clean gas from an MEA system may be below the 5 mol% level specified in the NREL design. Since the CO₂ content in the clean gas is lower than the level that the synthesis catalyst can tolerate, the excess CO₂ removal is acceptable, but its cost is the additional regeneration energy and operating cost. Tertiary amines, on the other hand, absorb more H₂S and less CO₂ compared to primary and secondary amines due to the solvents' selectivity for H₂S. Preliminary process modeling of an MDEA system indicates that in order to meet the specified 5 mol% CO₂ in the clean syngas, the amount of H₂S removed may be more than necessary, resulting in a clean gas stream with an H₂S concentration below the 50 ppmv level required for catalyst activity. In such case, the clean gas stream could be injected with a small amount of dimethyl disulfide in order to control the H₂S content. The cost of dimethyl disulfide injection is not expected to be significant due to the small quantities required; thus, the economic impact on the overall plant should be marginal.

Lower MDEA circulation rate and heat of regeneration – Preliminary analysis, using data shown in Table 3-1, was also carried out to evaluate the circulation rate and heat of regeneration of the MDEA system to achieve the required acid gas removal for the NREL design (i.e., removal of 3.4 lbmol/hr H₂S and 1,195 lbmol/hr CO₂). An average acid gas pickup and solution concentration from Table 3-1 is used, and the estimated regeneration energy is based only on the heat of reaction. Results are shown in Table 3-2. Of the various amine solvents compared, MDEA has the lowest circulation rate and regeneration energy, which should result in the most economical plant design. A more detailed study would be needed to clearly define its comparative advantages.

Demonstrated MDEA commercial experience - none of the amine processes has been demonstrated on a commercial scale with biomass-derived syngas, but MDEA has been successfully used in commercial IGCC application to treat coal-derived gases. This, coupled with the other factors cited above, would suggest that it should be a good candidate for the NREL biomass-derived syngas clean up application.

Table 3-1 Chemical Absorption Processes Summary Table

	Monoethanolamine (MEA)	Diethanolamine (DEA)	Diglycolamine (DGA)	Diisopropanolamine (DIPA)	Methyldiethanolamine (MDEA)
Amine MW	61.08	105.14	105.14	133.19	119.16
Solvent Capabilities for Gas Treating					
Minimum Acid Gas in Treated Gas, ppmv					
H ₂ S ^[3]	1	4	1-4	10	10
CO ₂ ^[3,4]	15	200	15	30%-90% removal	Bulk removal only
Selective H ₂ S Removal ^[5]	No	No	No	Some	Yes
Removal of COS, CS ₂ , and Mercaptans ^[4,5]	Partial (Note 1)	Partial	Partial	COS only	Slight (Note 1)
Solution Subject to Degradation ^[4,5] (Degrading Species)	Yes (CO ₂ , COS, CS ₂)	Some (CO ₂ , COS, CS ₂)	Yes (CO ₂ , COS, CS ₂)	Some (CO ₂ , CS ₂)	No
Approximate Operating Parameters					
Solvent Concentration in H ₂ O, wt%	15-25 ^[5]	25-35 ^[5]	40-60 ^[2]	20-40 ^[3]	40-60 ^[2]
Acid Gas Pickup, SCF/gal @ 100°F	3.1-4.3 ^[5]	3.8-5.0 ^[5]	4.7-6.6 ^[5]	2.4-8.1 ^[3]	3.8 ^[3]
Moles/mol amine	0.33-0.40 ^[5]	0.35-0.65 ^[5]	0.25-0.30 ^[5]	0.38-1.1 (Note 2)	0.2-0.55 ^[4]
Average Heats of Reaction, Btu/lb					
H ₂ S ^[2]	615	510	675	475	520
CO ₂ ^[2]	825	700	820	720	575
Typical Utility Demands					
LP Steam, lb/gal ^[3]	0.8-1.5	0.7-1.1	1.5	0.7-0.8	1.0
Typical Solvent Losses, lb/MMSCF Sweet Gas ^[3]	2-4	1-2	2-4	2-4	1-2

Notes:

(1) Primary amines are the most reactive with COS and CS₂ while tertiary amines are the least reactive. Comparatively, COS and CS₂ removal would be the least with tertiary amines.

(2) Moles AG/mol amine values for DIPA are calculated from the SCF/gal acid gas pickup data using a 30 wt% solution. The calculated acid gas pickup rate is used for the preliminary circulation rate estimation in Section 3.2. The acid gas pickup rate at the upper range is generally applicable for applications with high H₂S partial pressures. For CO₂ removal applications, the formation of carbamate limits the solution capacity; thus, the acid gas pickup rate is limited to 0.5 mol CO₂/mol amine.

Table 3-1 (Continued)

	Monoethanolamine (MEA)	Diethanolamine (DEA)	Diglycolamine (DGA)	Diisopropanolamine (DIPA)	Methyldiethanolamine (MDEA)
Commercial Experience With Synthesis Gas With Natural and Refinery Gas	Yes	Yes	Yes	Yes Yes	Yes Yes
Process Advantages	Often the preferred solvent for treating gases containing only H ₂ S and CO ₂ in low concentrations	(1) Partial COS removal attainable without significant solution degradation; (2) Suitable for low-pressure operations due to low solvent vapor pressure	(1) Partial COS removal; (2) Lower solvent circulation rate and steam consumption compared to MEA	(1) Partial COS removal attainable without significant solution degradation; (2) Low regeneration steam required	(1) Highly selective; (2) Low heats of solution, resulting in low regeneration duty; (3) Solvent has excellent thermal and chemical stability and is noncorrosive
Process Disadvantages	(1) Not suitable for treating gases with high COS and CS ₂ concentrations due to formation of nonregenerable products, resulting in appreciable solution losses; (2) High heats of solution, requiring high regeneration energy; (3) Solution more corrosive compared to other amine solutions	Vacuum distillation may be necessary for reclaiming of contaminated solutions ^[2]	High heats of solution, requiring high regeneration energy	Not widely used in U.S.	

Table 3-2 Estimated Amine Circulation Rates and Regeneration Energy for NREL Design

Solvent Type	MEA	DEA	DGA	DIPA	MDEA
Acid Gas Pickup, mol AG/mol amine	0.37	0.50	0.28	0.50	0.38
Solution Concentration, wt%	20%	30%	50%	30%	50%
Circulation Rate, gpm	1,971	1,540	1,732	2,127	1,463
Regeneration Energy, MMBtu/hr (based on heats of solution only)	43	37	43	38	30

4.1 PROCESS OVERVIEW

Physical absorption processes use an organic solvent to absorb the acid gases from raw gas streams without chemical reaction. Each component in the raw gas stream is absorbed in proportion to its concentration and solubility. The driving force of this process is the high solubility of acid gases in the organic solvent. In most cases, solubility increases with increasing pressure and decreasing temperature. Thus physical absorption process is most efficient and economical when operated at the highest pressure and lowest temperature possible.

Physical absorption has three advantages compared to chemical absorption. First, unlike most chemical absorption processes in which selective recovery may be difficult due to the simultaneous reactions of CO_2 and H_2S with the solvent, selective H_2S removal can be achieved with physical absorption processes since H_2S has a higher solubility than CO_2 in most organic solvents. Selective H_2S removal is necessary when the $\text{H}_2\text{S}/\text{CO}_2$ ratio in the feed gas stream is too low—a result when the raw gas has little H_2S and a large amount CO_2 —to produce an acid gas stream with a high enough H_2S content to be processed in the conventional Claus sulfur recovery unit. The $\text{H}_2\text{S}/\text{CO}_2$ ratio can be increased by selectively removing the H_2S to concentrate the sulfur content in the acid gas stream.

Second, minor gas impurities such as COS and mercaptans are soluble in most organic solvents, making removal of such impurities in the acid gas removal unit possible without subjecting the solvent to degradation. Due to the chemically inert nature of physical solvents, solvent deterioration from irreversible reactions with gas impurities is not an operating concern.

Third, the organic solvents can be regenerated by pressure reduction, inert gas stripping, or thermal regeneration. Pressure reduction and inert gas stripping require little use of energy while thermal regeneration requires significantly less energy compared to that of chemical absorption processes due to the lower heat of desorption of acid gases. When stringent H_2S purity is required in the treated gas, thermal regeneration is used to achieve thorough stripping of the rich solvent.

However, the benefits of the physical absorption processes may be offset by several of their disadvantages. These processes usually require high operating pressures, high acid gas partial pressures, and low operating temperatures to obtain economic solvent loading since the solvent loading capacity improves at higher acid gas partial pressures and lower operating temperatures. As a result, the capital and operating costs of the physical absorption processes are generally higher compared to those of the amine processes, contributed by the high-pressure equipment and the additional heat exchange equipment and refrigeration required to achieve reduced operating temperatures.

Additionally, hydrocarbons are soluble in most organic solvents to some degree, with heavier hydrocarbons more soluble than lighter ones. For this reason, physical absorption processes are not economical when there are high concentrations of hydrocarbons in the raw gas due to appreciable product losses.

Below are brief descriptions of the two commonly used physical solvent-based AGR processes: Selexol and Rectisol. Their characteristics and performance are summarized in Table 4-1.

Selexol

The Selexol process has been used for acid gas removal in a wide range of applications including natural gas processing, ammonia and hydrogen production, and petroleum and coal gasification^[2]. The solvent used in the Selexol process is a mixture of a dimethylether of polyethylene glycol. The Selexol solvent has high capacity for acid gases, favorable solubility for acid gases versus other light gases, and high selectivity for H₂S over CO₂. It also has low vapor pressure, which minimizes solvent losses, and is chemically and thermally stable, which eliminates the need for reclaiming or purging. Due to the solvent's inert chemical characteristics, the Selexol process uses carbon steel as the standard material of construction, except for areas that are exposed to CO₂/H₂S evolution where stainless steel is used.

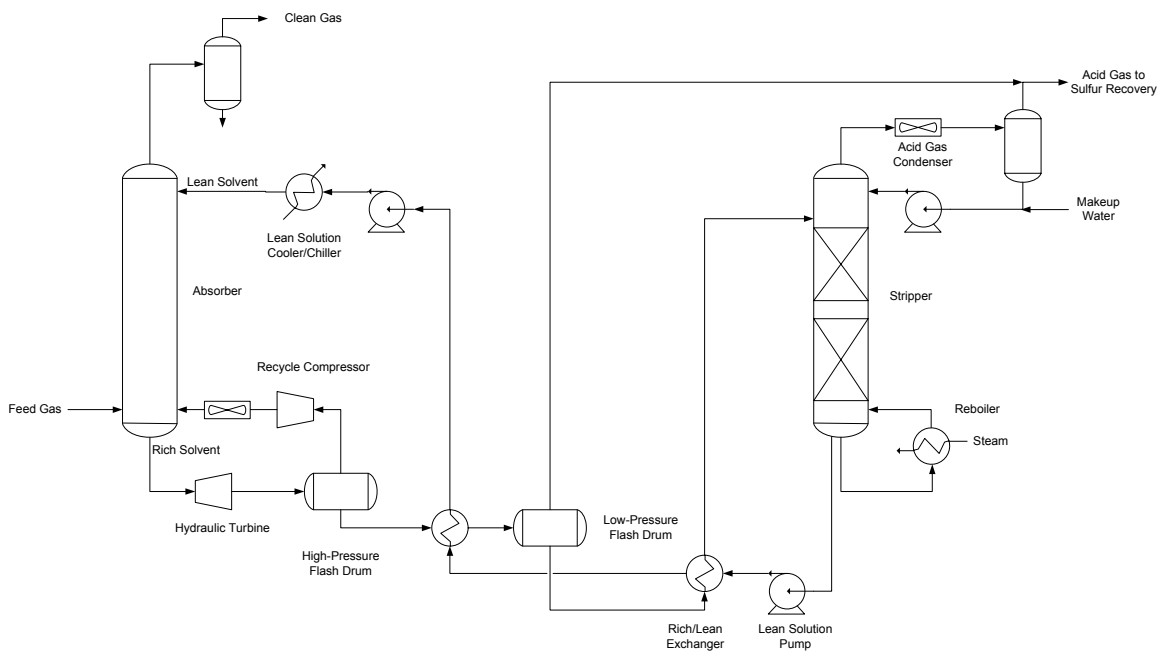
The Selexol process can be configured in a number of ways, depending on the levels of acid gas removal required, from selective H₂S or bulk CO₂ to trace acid gas removal. For selective H₂S removal, refrigeration is normally not used, but it is necessary when CO₂ removal is also required. Figure 4-1 illustrates a Selexol process for the removal of H₂S and CO₂. The feed gas is contacted countercurrently with a lean solvent in an absorber at high pressure and lower temperatures so that H₂S and CO₂ are absorbed into the solvent. The rich solvent is regenerated by pressure reduction through a series of flash drums, followed by thermal regeneration with steam stripping. The high-pressure flash gas vapors, consisting mostly of hydrogen and CO, are compressed and returned to the absorber. The low-pressure flash gas vapor is combined with the acid gas stream from the stripper overhead. The combined stream is sent to the sulfur recovery unit for processing. The lean solution is either cooled or chilled, depending on the level of CO₂ removal, and returned to the top of the absorber.

Figure 4-2 shows the basic flow configuration of a selective Selexol process, where removal of H₂S and CO₂ can be accomplished via two separate absorbers.

Table 4-1 Selexol Solvent Relative Solubility of Gases

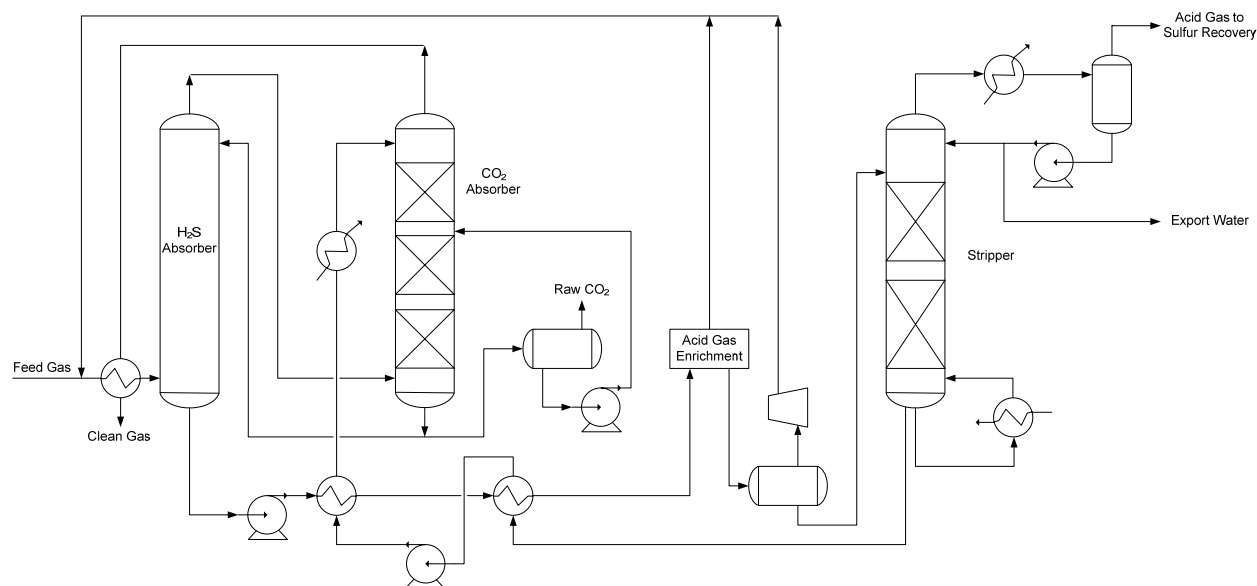
<u>Compounds</u>	<u>Solubility Ratio</u>
H ₂ (Least Soluble)	1.0
N ₂	1.5
CO	2.2
CH ₄	5
CO ₂	75
COS	175
H ₂ S	670
CH ₃ SH	1,700
SO ₂	7,000
H ₂ O	55,000
HCN (Most Soluble)	95,000

Source: Reference [6]



Source: Adapted from reference [6]

Figure 4-1 Typical Selexol Process Flow Diagram



Source: reference [15]

Figure 4-2 Typical Selective Selexol Process Flow Scheme

Rectisol

The Rectisol process, which uses chilled methanol as a solvent, is distinctive from other physical absorption processes in that it can remove H_2S and CO_2 as well as other gas impurities such as HCN and organic sulfur compounds to very low levels—with H_2S concentration as low as 0.1 ppm and CO_2 concentration of just a few ppm. Depending on process requirements, the Rectisol process can be designed in various configurations to achieve (1) deep, nonselective CO_2 and H_2S removal, (2) selective H_2S removal with some degree of CO_2 slippage, or (3) selective removal and recovery of separate CO_2 and H_2S products, along with the treated product gas stream.

The Rectisol process operates at very low temperatures, ranging from -40°F to -100°F . Low temperatures enhance solvent solubility and reduce solvent losses, which can be significant due to the relatively high vapor pressure of methanol. However, operation at low temperatures requires additional heat exchange equipment and high refrigeration energy, which contributes to high plant costs relative to other processes. For this reason, the Rectisol process is mostly used when stringent purity of the treated gas is required.

4.2 PROCESS APPLICABILITY TO THERMOCHEMICAL ETHANOL SYNTHESIS

In NREL's current design, the raw gas enters the AGR at 420 psia has an H_2S partial pressure of 0.1 psia and a CO_2 partial pressure of 48 psia. As shown in Figure 2-1, the total acid gas pressure of the feed gas is high enough that physical solvent processes of both Selexol and

Rectisol can be considered for the NREL application. For these processes, the issue of chemical incompatibility with the impurities in the feed gas, which consist of mostly CO₂ and H₂S, and a small amount of ammonia, is not a concern due to the chemically inert nature of the treating solvents. The required specifications of the treated gas are 50 ppmv H₂S and 5 mol% CO₂, which correspond to a required acid gas removal of about 79% H₂S and 59% CO₂. Given that deep H₂S and CO₂ removal is not required, the Selexol process would be the preferable option on the basis of relative plant cost. The capital cost of the Rectisol process is generally higher relative to the Selexol process due to the need for more heat exchange equipment to cool the absorber feed gas and to recover the cold duty from the product gas. The operating costs are also generally higher than the Selexol process as a result of higher power requirements due to colder refrigeration temperatures.

Similar to the MDEA system, preliminary simulation modeling of a Selexol process indicates that in order to meet the specified 5 mol% CO₂ in the treated syngas, the amount of H₂S removed may be more than necessary due to the H₂S selectivity of the Selexol solvent. Under this situation, the H₂S content of the treated syngas can be maintained at the required 50 ppmv level for ethanol synthesis catalyst activity by injection with a slip stream of dimethyl disulfide. Alternatively, the Selexol system can be designed for selective H₂S and CO₂ removal, which should offer a better control of the overall end product treated syngas composition.

Physical solvents have high affinity for hydrocarbons and CO. The NREL AGR feed gas stream contains a high concentration of CO and small quantities of hydrocarbons, ranging from methane to pentane, benzene and tar, which would be absorbed to some extent into the treating solutions. The loss of CO through absorption, if significant, would negatively affect the yield of the alcohol synthesis process and the overall plant efficiency.

Equally important, the absorption of CO and hydrocarbon gases into the treating solvents has an environmental impact on the overall process since these gases, which exit the AGR unit with the acid gas stream, would be vented with the CO₂ stream from the LO-CAT sulfur recovery unit (Figure 1-1, Section 1). The incineration of the CO₂ vent gas to destroy the CO and hydrocarbons would consume a significant amount of product gas as fuel as well as increase the overall plant cost.

The concentrations of CO (a criteria pollutant) and hydrocarbons (greenhouse gases) in the CO₂ vent stream can be minimized by depressuring the rich solution and recycling the flashed gas to the absorber. The flash pressure can, however, influence the level of contaminant in the CO₂ vent gas. At low flash pressures, less CO and hydrocarbons will be present in the CO₂ vented stream, but the cost for recycling the flashed offgas to the absorber would increase and can negatively impact the overall process economics. In comparison to an MDEA system, a physical solvent system is expected to have higher concentrations of CO and hydrocarbons in the vented stream. Preliminary process simulation of this effect was performed and the results are shown in Figure 4-3. The allowable CO and hydrocarbons concentrations in the CO₂ vent stream are site-specific and need to be established prior to the start of Task 2 detailed analysis.

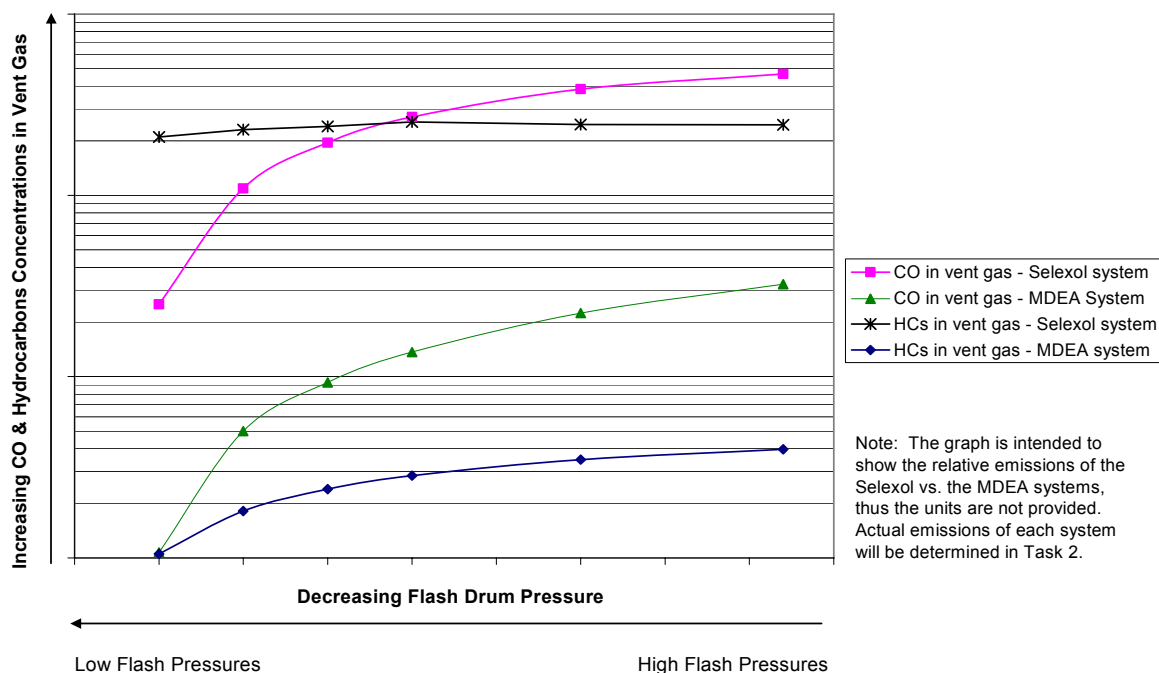


Figure 4-3 Order-of-Magnitude Comparison of CO and Hydrocarbons Absorption in a Selexol and MDEA Process

A Selexol plant, in general, is more costly than an equivalent size MDEA unit. Two main factors influencing the costs of the Selexol process are the solvent loading rates and the required refrigeration. First, the solvent loading rates of physical solvents are generally slower due to the higher solvent viscosity at low temperatures; thus, the absorption of acid gases into the treating solvent requires longer contact time and the use of more absorber stages. Accordingly, the Selexol process requires taller absorber column designs as compared to those of the amine systems, resulting in relatively higher capital costs. Second, although the steam requirements of the Selexol process would be lower due to the lower regeneration energy, refrigeration is required, incurring additional capital and operating costs. Therefore, compared to a MDEA, the plant cost of the Selexol process is expected to be higher at the given operating conditions.

Economics of the Selexol process may improve with increasing operating pressures. In NREL's current design, the raw gas enters the AGR unit at about 420 psia, and the treated gas is further compressed to the alcohol synthesis pressure of about 990 psia. If the Selexol process is operated at a higher pressure, the acid gas solubility will be enhanced, which will result in reduced solvent circulation rate, smaller absorber column size, and lower refrigeration load. At the higher operating pressure, however, the absorption of product gases will also increase, which would impact the CO and hydrocarbons emissions from the LO-CAT unit as well as the overall plant efficiency. The techno-economics analysis for the AGR process selection must also take this compression effect into consideration.

Table 4-2 Physical Absorption Processes Summary Table

	Selexol	Rectisol
Solvent Capabilities for Gas Treating		
Minimum Acid Gas in Treated Gas, ppmv		
H ₂ S	1 ^[6]	0.1 ^[7]
CO ₂	300 ^[3]	10-100 ^[7]
Selective H ₂ S Removal ^[2]	Yes	Yes
Removal of COS, CS ₂ , and Mercaptans ^[6,7]	Partial	Yes
Solution Subject to Degradation ^[4,8]	No	Not Reported
Approximate Operating Parameters		
Active Ingredient	Dimethylether of polyethelene glycol	Methanol
Acid Gas Solubility,		
CO ₂ Vol/Vol Solvent @ 1 atm ^[2]	3.63	8-15
H ₂ S Vol/Vol Solvent @ 1 atm ^[2]	32.4	41-92
Typical Solvent Losses, lb/MMSCF Sweet Gas ^[3]	0.5	
Commercial Experience with Gasification (Coal & Petcoke)	Yes	Yes
Process Advantages	Process used in a wide range of industries	Able to handle difficult treating conditions where other processes may not be suitable.
Process Disadvantages	Hydrocarbon losses can be significant when treating hydrocarbon-rich gas streams	(1) Low levels refrigeration required (2) Hydrocarbons heavier than C ₃ + are absorbed with CO ₂ and H ₂ S and are difficult to recover ^[7]

5.1 PROCESS OVERVIEW

The concept of the hybrid process is to combine a chemical solvent (typically an amine) and a physical solvent in order to take advantage of the effects of both processes. The presence of a physical solvent enhances solution capacity at high acid gas partial pressures. However, this advantage is not observed at low acid gas partial pressures. The hybrid process can achieve very low acid gas specifications in a single treating step through a combination of bulk acid gas removal by the physical solvent and stringent purification by the chemical solvent.

A common hybrid process is the Shell's Sulfinol process, which is often used to treat refinery, natural, and synthesis gases. The Sulfinol solvent is a mixture of tetrahydrothiophene dioxide (Sulfolane), an alkanolamine (either DIPA or MDEA), and water. The solution with DIPA, referred to as Sulfinol-D, is usually selected when complete removal of H_2S and CO_2 as well as deep removal of COS is required. The Sulfinol-D solvent is used in the majority of the Sulfinol plants in operation worldwide. The solution with MDEA, referred to as Sulfinol-M, is usually used for selective removal of H_2S in the presence of CO_2 and is capable of partial removal of COS. Both solvents are capable of removing mercaptans to low levels^[2].

The Sulfinol process offers several advantages, including:

- Sulfinol systems are better suited than amine systems to treat gases containing mercaptans and COS since the amine systems cannot efficiently remove these compounds
- Sulfinol solvents are reported to have low solubility for hydrocarbons up to pentane. This is an advantage over the physical absorption systems when treating gases rich in hydrocarbons since hydrocarbon losses can be minimized
- Sulfinol solvents are stable. Solution degradation and losses are minimal
- Corrosion problems are not prevalent in Sulfinol plants
- High solution capacity at high acid gas partial pressures

Some disadvantages of the Sulfinol process are:

- At CO_2 acid gas pressure below 100 psia, the solvent loading (scf gas/gal solvent) of Sulfinol is worse than 15 wt% MEA^[13].
- At low H_2S partial pressure, the Sulfinol solution capacity is inferior to aqueous MEA^[2], but solution capacity improves as the H_2S partial pressure increases. A pronounced solution capacity enhancement is observed at H_2S partial pressure above 40 psia. Therefore, the Sulfinol process requires high operating pressures and high acid gas partial pressures to obtain the benefit of high solution capacity
- Sulfinol systems may incur royalty cost and higher solvent costs than amine systems.

5.1.1 Flow Scheme

The Sulfinol process flow scheme, shown in Figure 5-1, is similar to that of a conventional amine system with the inclusion of the flash tank to recover the absorbed hydrocarbons. The recovered hydrocarbons can either be recycled to the absorber or used as plant fuel.

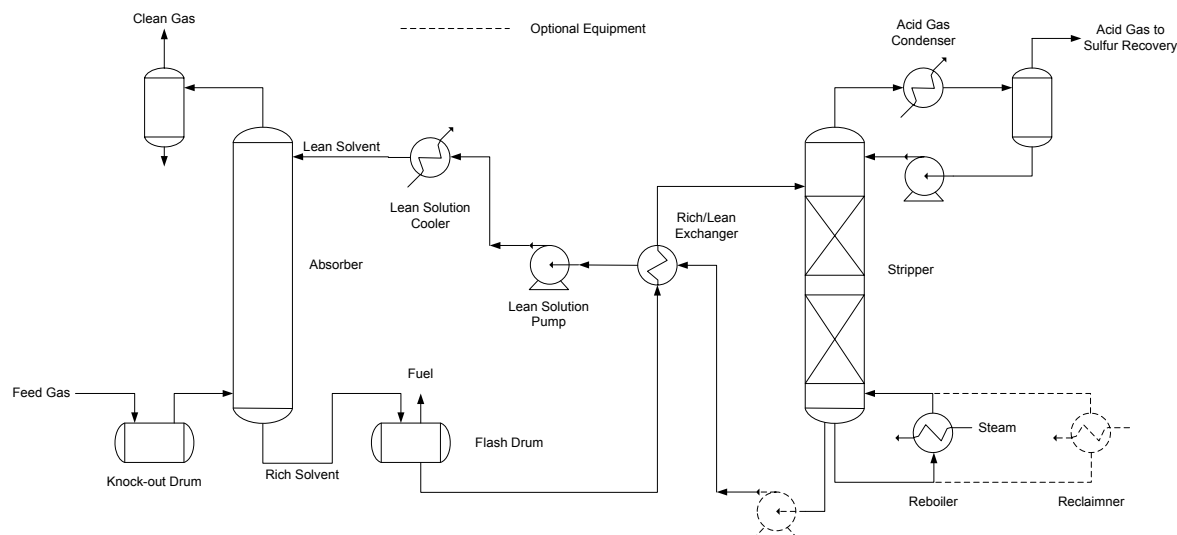


Figure 5-1 Typical Sulfinol Process Flow Diagram

5.2 PROCESS APPLICABILITY TO THERMOCHEMICAL ETHANOL SYNTHESIS

General guidelines, Figures 2-2 to 2-3, suggest that Sulfinol is best suited for H_2S removal, but not CO_2 (Figure 2-4). This, coupled with the reported findings of Edwards^[13] that the solvent loading of Sulfinol is worse than 15 wt% MEA at CO_2 partial pressure below 100 psi, would seem to suggest that there is no advantage of using a Sulfinol process for the NREL ethanol synthesis application.

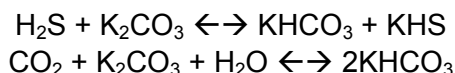
Hybrid system of mixed solvents tends to be highly proprietary, with its formulation heavily guarded by the technology developer/vendors. It is hard to carry out any design and economic assessment/evaluation without proper inputs from them. Furthermore, hybrid system may incur royalty cost and higher solvent costs than the amine systems.

Table 5-1 Hybrid Processes Summary Table

	Sulfinol-D	Sulfinol-M
Solvent Capabilities for Gas Treating		
Minimum Acid Gas in Treated Gas, ppmv		
H ₂ S	0.5-2 ^[3]	0.1 ^[3]
CO ₂	15-3000 ^[3]	5 ^[3]
Selective H ₂ S Removal ^[2]	Moderate	Yes
Removal of COS, CS ₂ , and Mercaptans ^[2]	Yes	Yes
Solution Subject to Degradation ^[2]	Minimal	Minimal
Approximate Operating Parameters		
Active Ingredient	Sulfolane, DIPA	Sulfolane, MDEA
Acid Gas Pickup, SCF/gal	4-16 ^[3]	
Typical Solvent Losses, lb/MMSCF Sweet Gas	0.5-1.6 ^[3]	
Typical Utility Demands		
LP Steam, lb/ MSCF AG Removed	0.5-1.2	
Commercial Experience		
With Coal Gasification	Yes	
With Other Gasification		
Process Advantages	(1) Capability for mercaptans and COS removal (2) Lower hydrocarbon solubility compared to physical absorption processes (3) Minimal corrosion and solution degradation (4) Solution capacity enhanced at high acid gas partial pressure	Same as Sulfinol-D
Process Disadvantages	(1) Solution capacity inferior to amine at low H ₂ S acid gas partial pressure (2) May incur royalty cost and higher solvent costs than amine system	Same as Sulfinol-D

6.1 PROCESS OVERVIEW

The hot potassium carbonate process—a chemical absorption process similar to the amine-based systems—has been used primarily for CO₂ removal from synthesis gas in ammonia and hydrogen plants, and also for acid gas removal in natural gas plants. The process uses an aqueous solution of potassium carbonate (K₂CO₃) to absorb CO₂ and H₂S. The rate of CO₂ absorption can be enhanced by increasing the CO₂ concentration, the solution alkalinity, or temperature^[2]. Organic sulfur compounds (COS, CS₂, and mercaptans) can also be removed to some extent. The potassium carbonate solution reacts with the acid gases as followed:



The three basic flow schemes for the potassium carbonate process are the single-stage process, the split-flow process, and the two-stage process, as shown in Figures 6-1, 6-2, and 6-3, respectively. Selection of a suitable configuration depends on the required purity of the treated gas. In the simplest configuration, illustrated by the single-stage process, the acid gas is absorbed in a countercurrent absorber by a lean potassium carbonate solution. The rich solution is regenerated by flashing, which releases approximately one third to two thirds of the absorbed CO₂^[4], and steam stripping in a low-pressure stripper. The stripping steam requirement is reduced as a result of an appreciable solvent regeneration by pressure reduction. The absorber and stripper normally operate at approximately the same temperature of 230-240°F^[5]. For this reason, the heat exchange operations between the lean and rich streams are eliminated.

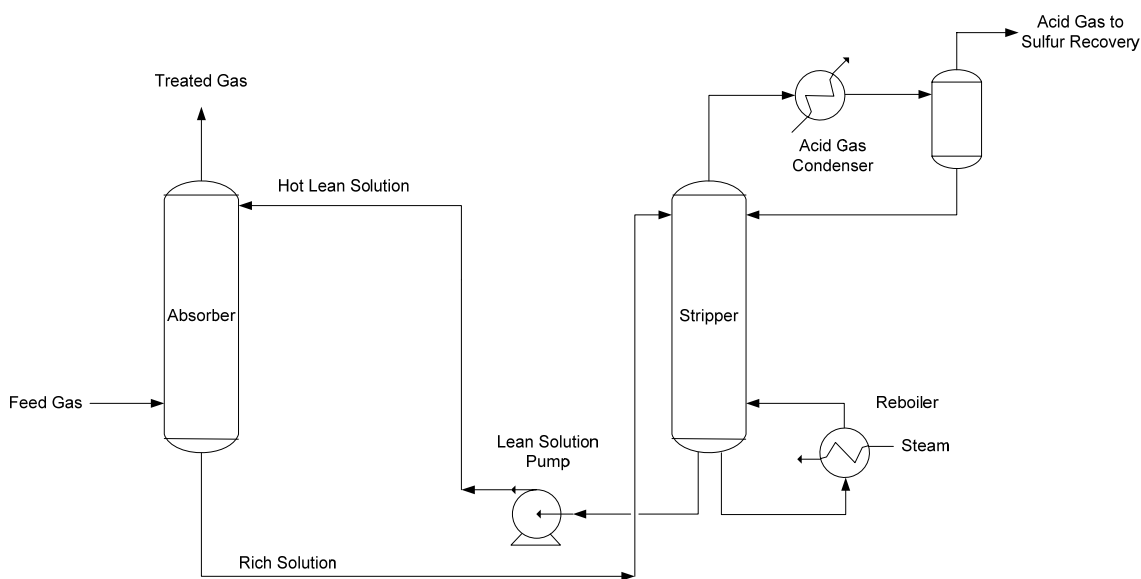
In the split-flow process, the lean solution from the stripper is split: a major portion of the hot solution is fed to the middle section of the absorber for bulk removal while the remainder is cooled and fed at the top of the absorber for trim acid gas removal. With this process modification or enhancement, the two-stage process can achieve more complete CO₂ removal. In this configuration, a major portion of the solution is withdrawn from the stripper at a point above the reboiler. Only a small portion of the solution passes down through the bottom of the stripper to the reboiler. Since this small portion of the solution is regenerated by the total steam supply to the stripper, it is thoroughly stripped and thus capable of removing the CO₂ to low levels. The thoroughly stripped solution is then cooled and fed to the top of the absorber.

The hot carbonate process offers several advantages, including:

- Lower regeneration energy requirements compared to that of the amine systems due to the low heat of solution for CO₂ absorption in potassium carbonate
- Less hydrocarbon absorption compared to the physical absorption processes due to low solubility of hydrocarbons in the potassium carbonate solution

The disadvantages of the process are:

- Corrosion is a problem for some portions of the plant, requiring the use of stainless steel
- At high temperatures, potassium carbonate reacts with CO to form potassium formate, which requires costly solvent purge and makeup. This problem can be controlled by lowering the absorber temperature, but at a cost of reducing the CO₂ absorption rate, which in turn, would lead to higher solution rate and regeneration energy.



Source: Adapted from Engineering Data Book (1987)

Figure 6-1 Typical Hot Potassium Carbonate Single-Stage Process

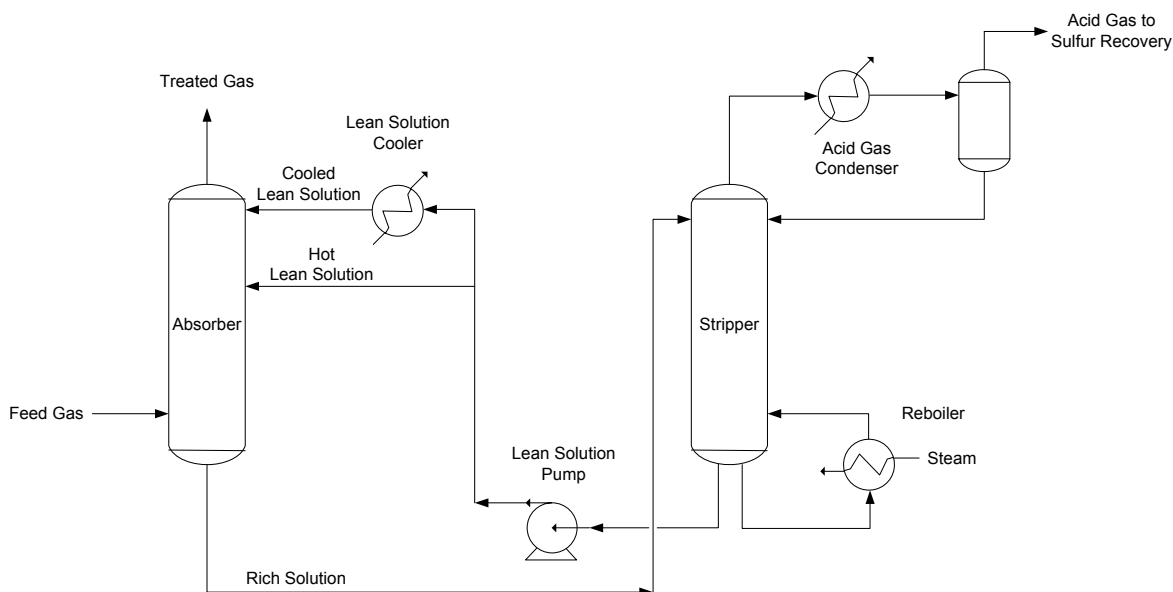
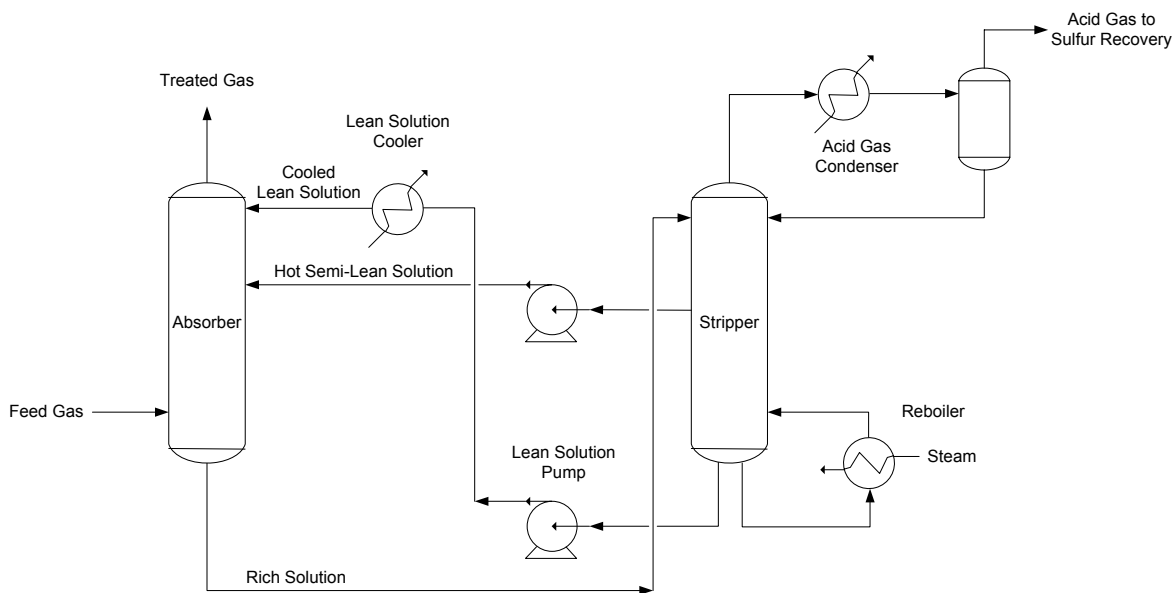


Figure 6-2 Typical Hot Potassium Carbonate Split-Flow Process



Source: Adapted from Engineering Data Book (1987)

Figure 6-3 Typical Hot Potassium Carbonate Two-Stage Process

Table 6-1 summarizes the performance and characteristic of the two popular hot carbonate processes: the Benfield process, licensed by UOP, and Catacarb process, licensed by Eickmeyer and Associates. The Benfield process uses an activated, inhibited hot potassium carbonate solution. Activators, either DEA or an organic activator known as ACT-1, are added to the solution to accelerate the rate of CO₂ absorption while inhibitors are used to minimize corrosion. The use of activators results in significant process improvements in terms of better product quality and lower capital and operating costs. The Benfield process has been widely used for H₂S and CO₂ removal from natural and ammonia synthesis gas. The process has a variety of configurations that permit process optimization and energy reduction.

Similar to the Benfield process, the Catacarb process also uses activators to catalyze the CO₂ absorption rate to improve product quality and lower plant costs. The two types of activators used in this process are organic or inorganic activators. Organic activators consist of amine promoters to improve acid gas absorption rate. Inorganic activators are used in oxidizing environments where the presence of oxygen in the feed gas may deteriorate organic components. Inhibitors are used to mitigate corrosion problems. The Catacarb process has primarily been used for CO₂ removal from synthesis gas, but it is also applicable for H₂S removal from natural gas. The process is available in a number of configurations, designed to provide high purity gas and greater heat economy.

6.2 PROCESS APPLICABILITY TO THERMOCHEMICAL ETHANOL SYNTHESIS

Hot potassium carbonate process has potential as an AGR candidate for NREL's process. The design syngas specification has significant amount of CO, which can cause design problems. At high concentration (design CO partial pressure of ~180 psia) CO has the potential to react with the potassium carbonate solution to form potassium formate at high temperatures, which would require costly solvent purge and makeup. Typical applications of the hot potassium carbonate processes in the hydrogen or ammonia plants normally have a CO partial pressure of less than 10 psia in the gas streams (after the CO shift step). Since the CO partial pressure of the syngas in the NREL design is considerably higher than this typical range, the hot potassium carbonate processes are not recommended, without addressing this issue in more detail with the technology vendors.

Furthermore, despite its seemingly simple chemistry, the hot carbonate-based AGR process is actually quite complicated and difficult to model with commercial process simulators. There are additional side reactors within the aqueous media, which are not well defined. The acid gas reactions involve many other ionic species. Unless there is a set of well defined and documented experiment and/or plant data for benchmarking, it is not certain to what extent the process performance can be truly captured. Any application design would most likely have to be involved directly with the technology vendors.

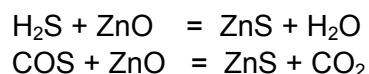
Table 6-1 Hot Potassium Carbonate Processes Summary Table

	Benfield	Catacarb
Solvent Capabilities for Gas Treating		
Minimum Acid Gas in Treated Gas, ppmv		
H ₂ S	4 ^[3]	4 ^[3]
CO ₂	500 ^[3]	500 ^[3]
Selective H ₂ S Removal	No	No
Removal of COS, CS ₂ , and Mercaptans ^[5]	Partial	Partial
Solution Subject to Degradation ^[5]	Minimal	Minimal
Approximate Operating Parameters		
Active Ingredient	K ₂ CO ₃ + Activator + Inhibitor	K ₂ CO ₃ + Activator + Inhibitor
Acid Gas Pickup, SCF/gal		
Typical Utility Demands		
LP Steam, lb/ MSCF AG Removed	90-160 ^[3]	35-55 ^[3]
Commercial Experience		
With Coal Gasification		
With Synthesis Gas from Catalytic Steam Reforming	Yes	Yes
Process Advantages	(1) Can achieve high purity gases (2) Lower regeneration energy than amines	(1) Can achieve high purity gases (2) Lower regeneration energy than amines
Process Disadvantages	Corrosion problems	Corrosion problems

7.1 PROCESS OVERVIEW

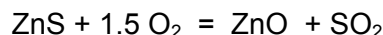
The RTI warm gas clean up (WGPU) process uses ZnO sorbent to remove H₂S from gas streams. The principal application of the process is for bulk removal of H₂S; CO₂ is not removed by the process. Presently, there are no significant commercial applications of this process.

RTI's WGPU process, being developed for high-temperature IGCC application, consists of two major system components: High Temperature Desulfurization process (HTDS) and Direct Sulfur Recovery process (DSRP). Figure 7-1 shows a simplified WGPU process scheme, located at the downstream of the coal gasifier. The HTDS process, consisting of a pair of fluidized bed reactors (identified as WGPU absorber & WGPU regenerator in Figure 7-1), is shown in Figure 7-2 in more detail. In the HTDS process, the hot raw syngas from the gasifier radiant boiler is first cooled to the operating temperature of the RTI WGPU absorber at approximately 800°F, via a fire tube convection boiler. In the process, high-pressure, saturated steam is generated. The raw syngas, mixed with a tail gas recycled stream, is then sent to a cyclone for bulk ash and char removal. The captured solids are recycled to the gasifier. The syngas leaving the cyclone is routed to the WGPU absorber where it is contacted with the circulating sorbent to remove H₂S and COS. The following reactions are believed to take place in the absorber:



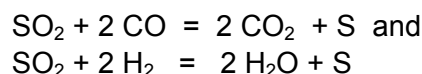
The regenerated sorbent from the regenerator, along with the recycled sorbent from the absorber stand pipe (Figure 7-2) enter the absorber near the bottom of the unit. Most of the sulfur absorption takes place in the absorber. The mixture leaves the top of the absorber into a cyclone where the solid sorbent containing ZnS is separated from the sulfur free syngas. Part of the solids is recycled to the absorber via a standpipe. A diverter valve located in the absorber standpipe takes a slip stream of these solids and feeds it to the regenerator.

Within the regenerator, the ZnS containing sorbent comes into contact with a mixture of oxygen and nitrogen at a pre-determined ratio. The oxygen then reacts with the ZnS and forms SO₂ according to the following reactions:



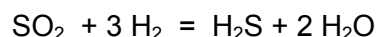
The above reaction is exothermic, raising the temperature of the resulting mixture to about 1300°F. A cyclone is used to separate the solids and recycled it to the absorber. The regenerator offgas containing SO₂ is heat exchanged with the incoming oxygen/nitrogen mixture before sending onto a companion DSRP (Direct Sulfur Recovery Process) unit for sulfur removal.

SO₂ and N₂ from HTDS regeneration, after heat exchanged cooling and filtration to remove entrained solids, are sent onto the fixed bed catalytic DSRP reactor where SO₂ is reduced to elemental sulfur according to the following reactions:



CO and H₂ are provided by a slip stream from the HTDS absorber. Approximately 98% of the SO₂ is converted to elemental sulfur in the DSRP reactor. The reaction is exothermic and it raises the reaction outlet mixture temperature to about 1,200°F. The product stream from the DSRP reactor is sent onto a two stage sulfur condenser unit where the elemental sulfur is condensed and separated. Heat is recovered by making low pressure steam.

The tail gas containing CO₂, N₂ and steam is directed to 2nd stage DSRP (Hydrogenation) reactor where the residual SO₂ is hydrogenated to H₂S in according with the following reduction reaction:



The hydrogenated stream is then cooled in two stages. In the first stage, the gas is cooled by generating low pressure steam. In the second stage the gas is further cooled to 315°F by heat exchange with boiler feed water (BFW). The cooled stream is then compressed and recycled as feed to the HTDS reactor.

Companion processes are included in the overall WGPU design, to remove mercury, chloride and ammonia to meet environmental emissions requirement, as follows:

- A high temperature dual candle filter system to remove entrained solids from the desulfurized syngas stream leaving the WGPU process before sending the stream onto the fixed-bed mercury removal vessel,
- High temperature (~ 550 °F) fixed-bed RTI proprietary mercury removal process,
- A companion high temperature (~ 550 °F) fixed-bed chloride guard bed for HCl removal, based on reaction with sodium bicarbonate in according with the following reaction –



- Inclusion of an SCR (Selective Catalytic Reduction) onto the power train for NO_x emissions control; thus no online ammonia removal is provided with the WGPU design.

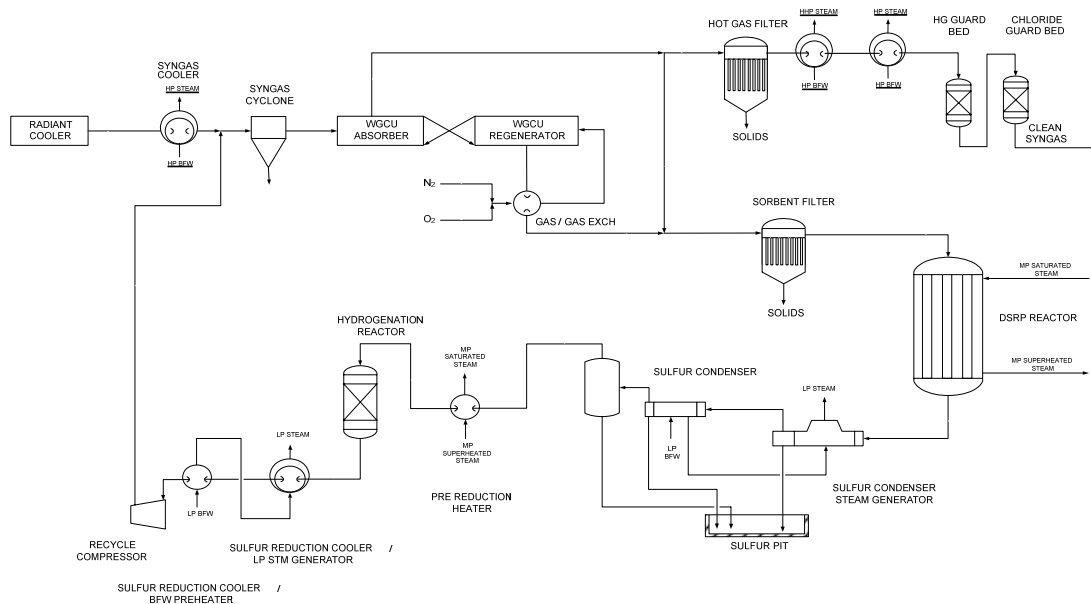


Figure 7-1 Simplified Overall WGSU Process Scheme

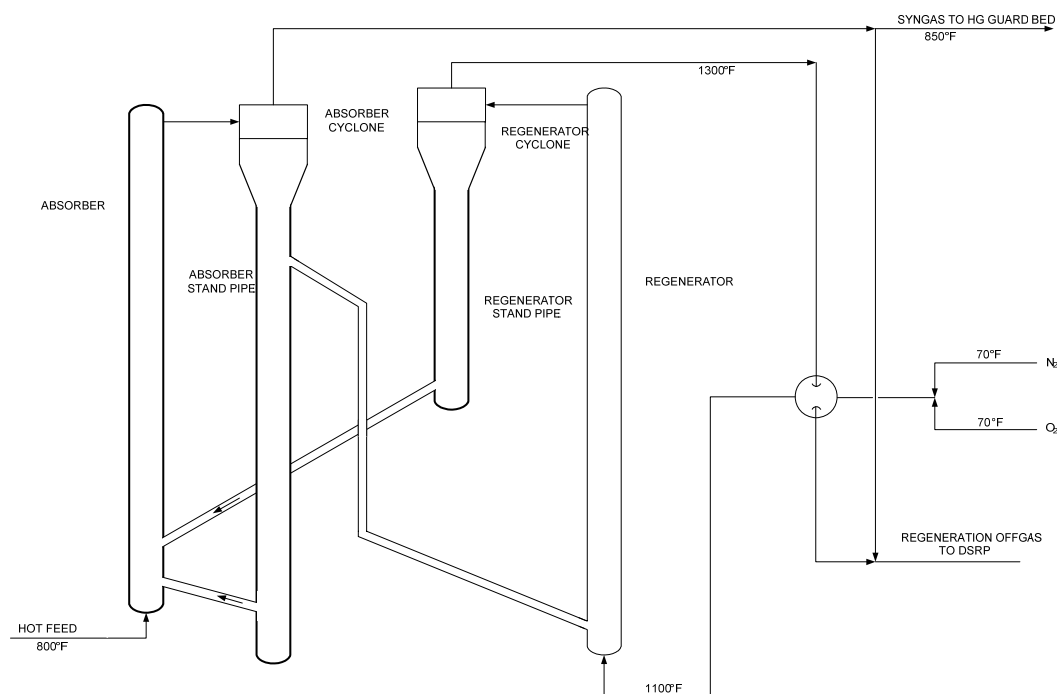


Figure 7-2 High Temperature Desulfurization (HTDS) Process Flow Scheme

7.2 PROCESS APPLICABILITY TO THERMOCHEMICAL ETHANOL SYNTHESIS

The WGPU process is being developed for coal gasification IGCC application to increase overall plant thermal efficiency. Principal application is for bulk sulfur removal and the process does not yet have the capability to remove CO₂. RTI is currently also developing a companion high temperature solid absorbent-based CO₂ removal process. At the current state of development, this process will not be able to meet the AGR requirement of the NREL design by itself.

8.1 PROCESS OVERVIEW

In the liquid phase oxidation processes, H_2S is absorbed and oxidized to elemental sulfur by oxygen carriers dissolved or suspended in a solution. The processes are generally used for H_2S removal from gases containing relatively low concentrations of H_2S in the presence of high concentrations of CO_2 . A high ratio of CO_2 to H_2S in the raw gas to a typical acid gas removal unit, such as an amine unit, can produce an acid gas stream with a H_2S concentration that is too low for processing in a conventional Claus sulfur recovery plant. In these cases, the liquid phase oxidation processes can be employed for sulfur removal and recovery. Generally, these processes are suitable for small-scale applications that require less than 20 tons per day of sulfur recovery capacity.

Liquid phase oxidation processes have several drawbacks. First, the process only removes H_2S and not CO_2 , thus by itself, it cannot serve as an AGR process for the thermochemical ethanol production. Second, the low solution capacities for H_2S and oxygen usually require large liquid circulation rates and large facilities to handle the precipitated sulfur. Third, the precipitated sulfur is difficult to separate from the solution. Finally, the heat generated by H_2S oxidation cannot be recovered for steam generation.

Popular liquid phase oxidation processes are the iron-chelate systems due to the non-toxic nature of the treating solutions. A common iron-chelate process presently used in commercial applications is the LO-CAT process. Below is a brief description of the LO-CAT process.

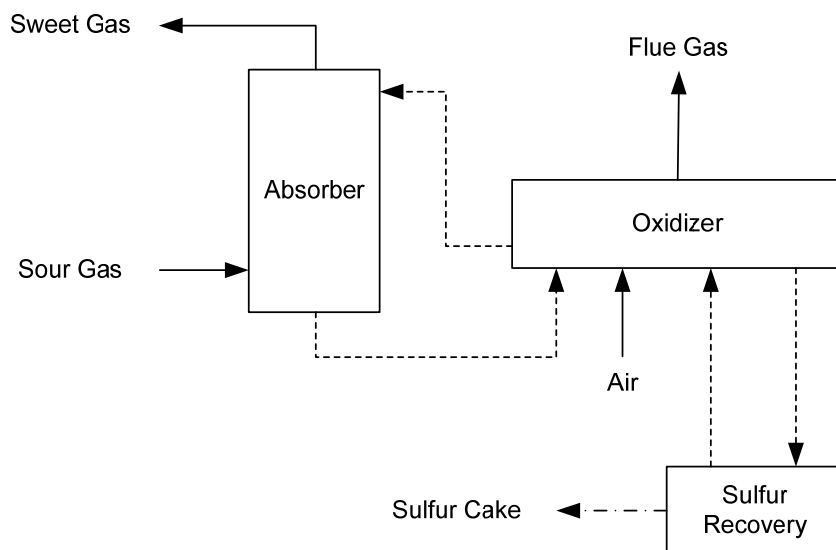
LO-CAT Process

The LO-CAT process uses iron catalyst held in a chelating agent to oxidize H_2S to elemental sulfur. The LO-CAT catalyst solution is environmentally safe and produces no hazardous waste byproducts. The process can be designed to achieve up to 99.9+% H_2S removal efficiency. The LO-CAT process has been used for H_2S removal from amine acid gas streams and synthesis gas from municipal solid waste gasification^[10].

Figure 8-1 illustrates a conventional LO-CAT unit. The process operates at ambient temperature and requires no heating or cooling of the solution^[2]. In the absorber, the H_2S in the gas stream is converted to elemental sulfur as it comes in contact with the LO-CAT solution. The spent catalyst and the elemental sulfur from the absorber are fed into the oxidizer where the spent catalyst is regenerated by contact with oxygen in air and the elemental sulfur is concentrated into a sulfur slurry. The sulfur slurry is then processed in the sulfur handling unit to recover the sulfur and any entrained catalyst. The recovered sulfur is considered low-value due to a small amount of entrained residual catalyst.

The capital cost of the LO-CAT system is largely determined by the solution circulation rate, which is directly proportional to the gas feed rate and its H_2S concentration and is inversely

proportional to the iron content in the solution while the operating costs are determined by the power and catalyst make-up requirements.



Source: Reference [11]

Figure 8-1 Conventional LO-CAT System

8.2 PROCESS APPLICABILITY TO THERMOCHEMICAL ETHANOL SYNTHESIS

The LO-CAT process is not a suitable option for the NREL acid gas removal application by itself because the process does not have the capability for CO₂ removal. However, the process is ideally suited for sulfur recovery as it is used in the current NREL design. As shown on Table 2-1 in Section 2, the feed gas to the amine unit has very little H₂S and a substantial amount of CO₂. As a result, the acid gas stream has a fairly low concentration of H₂S and cannot be processed in a conventional Claus sulfur recovery unit. Therefore, the LO-CAT system is used for sulfur recovery.

Table 8-1 Liquid Phase Oxidation Processes Summary Table

	LO-CAT
Solvent Capabilities for Gas Treating	
Minimum Acid Gas in Treated Gas, ppmv	
H ₂ S	10
CO ₂	Not removed
Removal of COS, CS ₂ , and Mercaptans	Not removed
Solution Subject to Degradation	Degrades by HCN ^[3]
Approximate Operating Parameters	
Active Ingredient	Chelated Iron
Feed Stream Acid Gas and Concentration Range, mol%	1.5-100 ^[3]
Typical Utility Demands	
Electricity, kWh/ MSCF AG Removed	234 ^[3]
Method of Regeneration	Air oxidation
Commercial Experience	
With Coal Gasification	Plant under construction
With Other Gasification	Yes
Process Advantages	(1) High sulfur removal efficiency (2) Non-toxic catalyst solution
Process Disadvantages	High solvent circulation rate

9.1 PROCESS OVERVIEW

Membrane separation systems are used primarily for bulk CO₂ removal in applications that have large flows, high CO₂ contents, or in remote locations. Membranes have been widely used in natural gas sweetening plants to remove CO₂ and water vapor and in enhanced oil recovery applications, in which CO₂ is removed from a natural gas stream and then reinjected into the oil well to enhance oil recovery.

The membrane systems are modular, skid mounted units that are capable of producing upward of 250 MMSCFD of treated gas ^[12]. The two types of membranes used are the spiral wound or hollow fiber membrane elements. The membrane elements are housed in pressure tubes that can be mounted in either a horizontal or vertical orientation. Selection of the type of membrane elements depends on the applications, and selection recommendations are normally provided by process vendors. In general, spiral wound elements, widely used in natural gas sweetening industry, can handle higher pressure and are more resistant to fouling. Hollow fiber elements have a higher packing density, which, in turn, lead to smaller plant size relative to the spiral wound-based plants.

Figure 9-1 illustrates a simple, single-stage membrane system for CO₂ removal, in which the feed gas diffuses through the membrane and is then separated into a permeate stream that is CO₂-rich, and a residual stream that is hydrocarbon-rich. The CO₂ flux, defined as the molar flow of CO₂ through the membrane per unit area of membrane, is dependent on the pressure drop across the membrane and on the CO₂ permeability. Permeability, in essence, is a measure of how quickly a gas can permeate through a membrane. It is a function of the solubility of CO₂ in the membrane and the diffusion coefficient of CO₂ through the membrane. Gases with high permeability, or fast gases (i.e. CO₂, H₂S, H₂, and water vapor), can permeate quickly through a membrane while gases with lower permeability, or slow gases (i.e. CO, methane, ethane, and other hydrocarbons), permeate at a much slower rate. Generally, separation of gases with high permeability requires less membrane area and thus, lower plant cost.

Another important variable of the membrane systems is selectivity, which is the ratio of the permeability of CO₂ to other components in the gas stream. Essentially, it is a measure of how much better the membrane permeates CO₂ compared to other compounds, such as hydrocarbons, in the gas stream. High selectivity of CO₂ over hydrocarbons results in limited hydrocarbons being permeated and consequently lower hydrocarbon losses.

Membrane systems offer several advantages, including:

- Low capital and operating costs for single-stage membrane systems. Multistage systems with large recycle compressors (see Figure 9-2) have comparable energy costs as traditional acid gas removal technologies.

- Operational simplicity. The one-stage systems have no moving parts. For the two-stage systems, the addition of the recycle adds some complexity.
- Reduced space requirements
- Ideal for remote locations
- Can be used to debottleneck existing solvent-based plant. In such cases, the membrane is used for bulk acid gas removal, and the existing solvent-based system is used for the final cleanup.

Disadvantages of the membrane systems include the loss of hydrocarbons and hydrogen products through permeation, which can be excessive in high CO₂ removal applications, and they are not suited for applications requiring deep acid gas removal.

9.1.1 Flow Scheme

Membrane systems can be configured in several variations, depending on the CO₂ removal requirements. The simplest flow scheme, a one-stage configuration, is showed in Figure 9-1. In high CO₂ removal applications, a two-stage system is used to reduce the hydrocarbons losses. In this flow scheme, the permeate stream from the first stage, which contains the hydrocarbons permeated with the CO₂, is recompressed and processed in the second stage. The permeate stream is at low pressure and thus requires recompression. The residue stream from the second stage, containing the recovered hydrocarbons, is recycled to the feed.

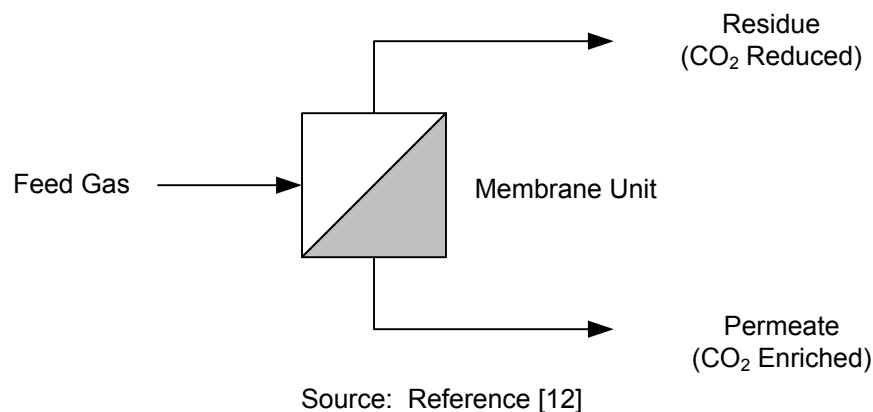


Figure 9-1 One-Stage Membrane System

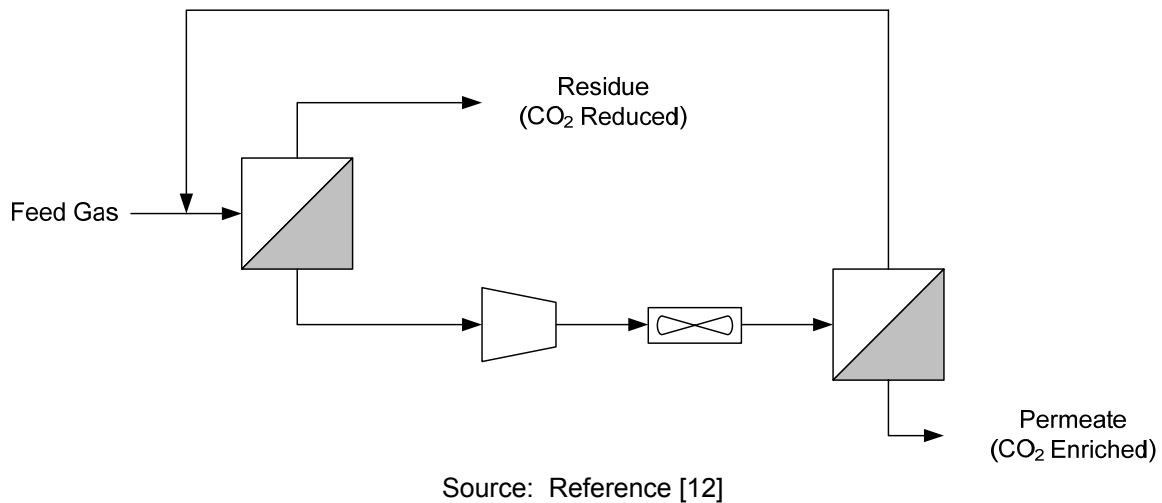


Figure 9-2 Two-Stage Membrane System

9.2 PROCESS APPLICABILITY TO THERMOCHEMICAL ETHANOL SYNTHESIS

Membrane separation systems are primarily used for CO₂ removal applications and do not have the capability to meet the H₂S removal requirement of the thermochemical ethanol process. Additionally, the raw gas in the NREL design has a high concentration of hydrogen, which has a high permeability; thus, the use of membrane for CO₂ separation can potentially result in substantial hydrogen losses.

Using the design basis provided by NREL, the screening criteria outlined in Section 2, and the survey performance of each AGR process, the qualitative process screening shows that the acid gas removal requirements for the thermochemical ethanol synthesis design can be achieved by the chemical and physical absorption processes. All other acid gas removal processes have limitations that make them unsuitable for the NREL design. Within the chemical absorption processes, the MDEA system appears to be the best option based its low circulation rate and regeneration energy requirement, which are the two primary factors that determine the capital and operating costs of an AGR process. Preliminary estimates of solution circulation rate and solvent regeneration energy requirements indicate that the MDEA system would have the lowest plant cost compared to the other amine systems.

The screening of the physical absorption processes indicates that the Selexol process would be more preferable than the Rectisol process since deep H₂S and CO₂ removal is not required. The Rectisol process, usually selected for deep or complete acid gas removal applications, generally has a higher plant cost than the Selexol process because of the additional heat exchange equipment and the higher power consumption required due to the lower refrigeration temperatures.

The screening analysis also indicates that the selectivity of the MDEA and Selexol solvents for H₂S in the presence of CO₂ may result in a clean syngas stream with an H₂S content that is below the 50 ppmv level required for synthesis catalyst activity. As discussed in the report, the H₂S concentration of the clean gas stream could be controlled by injection with dimethyl disulfide. The cost impact of such chemical injection is not expected to be significant since only a small quantity of dimethyl disulfide is required.

The screening analysis also indicates that in both the MDEA and Selexol systems, the absorption of product gases (CO and hydrocarbons) into the treating solvent has an environmental impact on the overall process since these gases would be vented with the CO₂ stream from the LO-CAT unit. As discussed in the report, the LO-CAT unit does not include CO₂ vent gas incineration, which would require a significant amount of product gas as fuel and also increase the overall plant cost. Therefore, any CO and hydrocarbons in the acid gas stream would be vented with the CO₂. The concentrations of CO (a criteria pollutant) and hydrocarbons (greenhouse gases) in the vented stream depend on the degree of product gas absorption and the level of product recovery achievable by flashing of the rich solution. The vented stream from the Selexol system would be expected to have higher concentrations of CO and hydrocarbons due to the higher solubility of such compounds in the Selexol solvent. Furthermore, in addition to the environmental impact, the loss of CO through absorption, if significant, would reduce the yield of the alcohol synthesis process, and thus, impacts the overall plant efficiency.

The qualitative cost comparison of the Selexol process with the MDEA process indicates that the Selexol process would have a higher plant cost at the given operating conditions and acid

gas partial pressures. The Selexol process may become more economical at higher pressures as a result of enhanced acid gas solubility. In the NREL design, the AGR unit can theoretically be operated between the ranges from the tar reformer pressure of 15 psia up to the alcohol synthesis pressure of 990 psia. For the Selexol process, which favors high operating pressures, a trade-off analysis is required to assess the power and cost penalties associated with the compression of syngas to high pressures. In this study, since all AGR options are qualitatively evaluated at the fixed operating pressure of 420 psia, the impact of syngas compression is not considered. Additionally, the increased solubility of CO and hydrocarbons in the Selexol solvent at high pressures must also be evaluated against the advantage of higher solution loading capacity resulting from improved acid gas solubility.

A detailed process design and cost estimation analysis of the MDEA system for thermochemical ethanol production is recommended in Task 2. In addition, a comparative study for the Selexol system, taking into consideration the various plant design parameters such as the overall syngas compression cost and the environmental impact of CO and hydrocarbons emissions requirement, etc., is also recommended.

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Task 2

Detailed MDEA Process Analysis

NREL Task Order No. KAFT-8-882786-01

September 2009

Prepared for:
United States Department of Energy / National Renewable Energy
Laboratory (NREL)

Contents

Section	Page
Executive Summary	1
Section 1 Introduction	4
Section 2 Methodology	5
Section 3 Design Basis	7
Section 4 Processes Description	12
Section 5 Analysis Results and Discussion	16
Section 6 Summary and Conclusions	27
References	28
Appendix A Case 1	29
Appendix B Case 2	33

Figures

Figure ES-1 Overview of NREL Thermochemical Ethanol Synthesis Process	1
Figure 4-1 Simplified MDEA Process Flow Diagram	15
Figure 5-1 Case 1 - MDEA Process Flow Diagram	17
Figure 5-2 Case 1 – Estimated Annual Cost of Sulfur Injection	19
Figure 5-3 Case 2 – Activated MDEA Process Flow Diagram	22
Figure 5-4 Case 2 – Estimated Annual Cost of Sulfur Injection	24
Figure 5-5 Effects of Ammonia on Utilities Requirements	26
Figure 5-6 Effects of Varying Acid Gas Concentrations on Utilities Requirements	26

Tables

Table ES-1 Summary of Analysis Results	2
Table 3-1 Feed Gas to the MDEA Unit	7
Table 5-1 Case 1 – Overall Utilities Requirements	18
Table 5-2 Case 1 – Variable Operating Cost Estimates	19
Table 5-3 Case 1 – Summary of Results	20
Table 5-4 Case 2 – Overall Utilities Requirements	23
Table 5-5 Case 2 – Variable Operating Cost Estimates	23
Table 5-6 Case 2 – Summary of Results	25
Table A-1 Case 1 – Detailed Utilities Requirements	30
Table A-2 Case 1 - Equipment List	31
Table A-3 Case 1 - Equipment Cost Estimates	32
Table B-1 Case 2 – Detailed Utilities Requirements	34
Table B-2 Case 2 - Equipment List	35
Table B-3 Case 2 - Equipment Cost Estimates	36

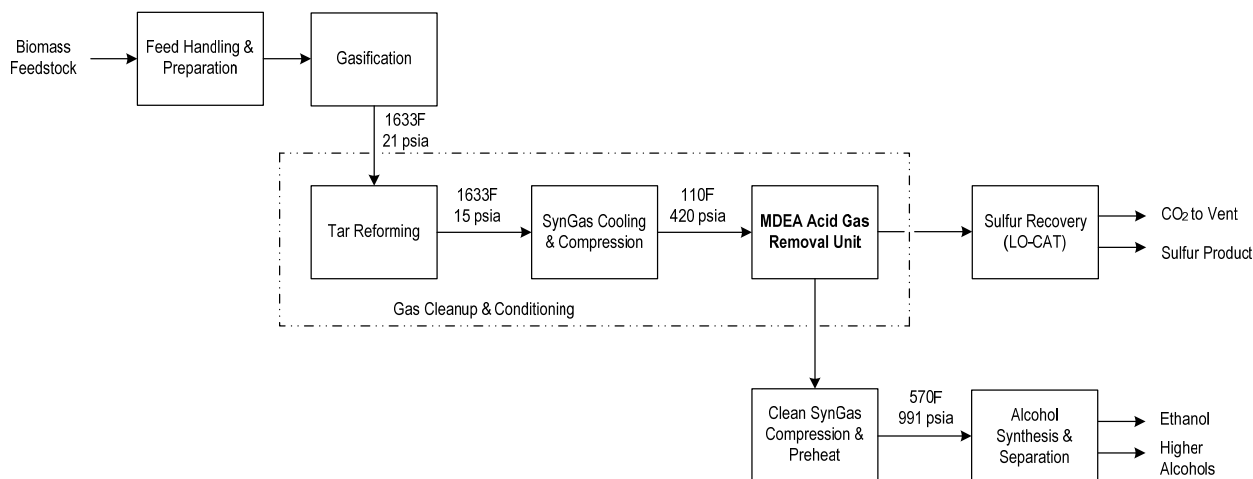
Acronyms

AGR	acid gas removal
BR&E	Bryan Research & Engineering
CWR	cooling water return
CWS	cooling water supply
DMS	dimethyl disulfide
MDEA	methyldiethanolamine
MM	million (1×10^6)
NREL	National Renewable Energy Laboratory
ppm	parts per million
ppmv	parts per million volume
SCF	standard cubic feet (1 atm, 60°F)

Executive Summary

In March 2009 NREL engaged Nexant to conduct a survey and screening of various acid gas removal (AGR) technologies in order to evaluate their capability to meet the specific design requirements for the NREL thermochemical ethanol synthesis process (Figure ES-1), and to recommend applicable acid gas removal options for a more detailed analysis. The results of the survey, documented in a report entitled “Task 1 - Acid Gas Removal Technology Survey and Screening for Thermochemical Ethanol Synthesis^[1]”, identified the MDEA and Selexol systems as suitable AGR options for the NREL design. As described in the Task 1 report, the gas cleanup conditioning process, of which the AGR unit is a part, has a significant impact on the overall plant economics since it has the highest cost component of all the process areas. Thus, the goal of this study is to provide a detailed design of an AGR unit so that NREL can better assess its technical and economic impacts on the overall process. NREL selected the MDEA system for the detailed analysis.

The detailed analysis of an MDEA unit consists of (1) the development of an MDEA process model using the Promax simulation software in order to obtain the heat and energy balance of the MDEA unit and (2) the cost estimation of the MDEA unit using the ICARUS software.



Source: Reference [2]

Figure ES-1 Overview of NREL Thermochemical Ethanol Synthesis Process

The MDEA system is designed to treat approximately 163 MMSCF of syngas containing 234 ppmv H₂S and 11.4 mol% CO₂. The required purity of the treated gas, which is dictated by the sulfur requirement and CO₂ tolerance of the alcohol synthesis catalyst, are 10 - 50 ppmv H₂S and 1 - 5 mol% CO₂. The amine solution used in the analysis is a generic 50 wt% MDEA solution. Additionally, since the NREL syngas has considerably higher CO₂ concentration than H₂S, a piperazine-activated MDEA solution to enhance CO₂ absorption is also evaluated. Piperazine is a promoter that is highly reactive towards CO₂; thus, when added to the MDEA

solution, the solution's capability for CO₂ absorption can be significantly enhanced. The results of the analysis, summarized in Table ES-1, show that:

Table ES-1 Summary of Analysis Results

<u>Design Feed Rates</u>		Case 1	Case 2
Amine Type		MDEA	Activated MDEA 50% MDEA/ 2% PZ
Amine Concentration	wt%	50	2%
Amine Circulation rate	gpm	1,534	1,374
Steam Consumption	klb/h	119	119
Power Consumption	kW	569	497
Make-up Water	gpm	40	43
Dimethyl Disulfide Consumption (Note 1)	gal/d	21-106	4-68
<u>Design Product Rates</u>			
Treated Gas	MMSCFD	153	153
Treated Gas H ₂ S Concentration	ppmv	0.13	18.16
Treated Gas CO ₂ Concentration	mol %	4.95	4.92
Heat Duty per lb Acid Gas Removed	Btu/lb	2,053	2,053
<u>Capital & Operating Costs</u>			
Total Installed Equipment Cost, (2Q09)	million \$	11.6	9.7
Annual Operating Costs (min) (Note 2)	thousand \$	260.9	145.9
Annual Operating Costs (max) (Note 2)	thousand \$	1,044.7	736.6

Notes:

- (1) The range of operating costs shown represents the minimum and maximum levels of DMDS injection required in order to maintain the H₂S content of the clean gas between 10 – 50 ppmv.
- (2) The minimum and maximum operating costs shown reflect the level of DMDS consumption
 - Case 1 – with the use of a generic MDEA solution, which has high selectivity for H₂S, the level of H₂S removal would have to be higher than necessary in order to meet the CO₂ specification in the clean gas. Thus, the H₂S content in the clean gas is lower than the required specification. In this case, the H₂S content of the clean gas can be controlled between 10 and 50 ppmv—the concentration necessary to maintain catalyst activity—by injection of dimethyl disulfide (DMDS) into the clean gas stream. DMDS is commonly used as a sulfiding reagent in industrial applications to control catalyst activity. The annual operating costs of the unit can vary considerably, as shown in Table ES-1, depending on the consumption requirement of DMDS. Thus, it is desirable to maintain the H₂S content of the clean gas at a concentration in which the operating cost can be minimized while preserving the catalyst activity. Catalyst vendors should be consulted for recommendations of the optimal H₂S content in the

clean gas. The total installed equipment cost for the MDEA unit in this case is 11.6 million dollars.

- Case 2 – with the use of piperazine as a promoter in the MDEA solution, the solution's capability for CO₂ absorption is significantly enhanced, resulting in 10% lower amine circulation rate and smaller absorber size for the MDEA unit as compared to Case 1. Consequently, due to the smaller plant size of the MDEA unit utilizing an activated MDEA solution, the total installed equipment cost, at 9.7 million dollars, is approximately 16% lower compared to the unit using a generic 50 wt% solution. Additionally, the study shows that as the solution's capability for CO₂ absorption increases, its capacity for H₂S absorption decreases. Thus, the H₂S content in the clean gas is higher compared to Case 1. Since the achieved H₂S purity of 18 ppmv in the clean gas meets the minimum requirement, less DMDS would be required to maintain the H₂S content between 10 - 50 ppmv. Depending on the level of DMDS consumption, the operating costs of the MDEA unit in this case are 30 to 45% lower compared to those in Case 1.
- Effects of the presence of ammonia in the feed stream on the MDEA unit – The sensitivity analysis shows that presence of ammonia in the feed gas significantly increases the duties of the stripper reboiler by 25% and the condenser by 45%, as compared to the feed gas with no ammonia present. Equally important, the presence of ammonia eventually leads to buildup in the stripper overhead system and contributes to corrosion. To minimize ammonia buildup, purging of the reflux water is necessary.

Thus, the results of the detailed analysis indicate that for the NREL thermochemical ethanol synthesis application, in which the syngas that has appreciable CO₂ and low H₂S concentrations, the MDEA unit utilizing an activated MDEA solution has more economics advantages over the one utilizing a generic MDEA solution. The use of a piperazine-activated MDEA solution enhances the rate of CO₂ absorption which results in a smaller plant size, and consequently lower capital and operating costs. Moreover, in order to minimize the impact of ammonia on the unit's operating costs, maximum removal of ammonia upstream of the AGR unit is critical.

1.1 INTRODUCTION

In March 2009 Nexant conducted a survey and screening of various acid gas removal (AGR) technologies to identify suitable acid gas removal options for the NREL thermochemical ethanol synthesis process and recommended the MDEA and Selexol systems for further detailed analysis. NREL selected the MDEA system for the detailed analysis in this Task 2 study.

The objective of Task 2 study is to provide a detailed design analysis of the MDEA process for H₂S and CO₂ removal. The feed gas to the MDEA unit and the clean gas specifications are provided by NREL. The detailed analysis consists of (1) the development of an MDEA process model using the Promax simulation software in order to obtain the heat and energy balance of the MDEA unit and (2) the cost estimation of the MDEA unit. This study evaluated a generic MDEA solution as well as an activated MDEA solution, which contains piperazine to enhance CO₂ absorption. The two cases evaluated in this study are:

Case 1 – Generic MDEA

Case 2 – Activated MDEA

Additionally, a sensitivity analysis was also performed to determine the impact of ammonia and of varying acid gas concentrations in the feed gas on utilities requirements of the unit.

The methodology and approaches used to develop the ProMax model and the capital cost estimate for the MDEA unit are described in the following sections.

2.1 PROMAX MODELING METHODOLOGY

ProMax simulation software was used to develop the process model for the MDEA unit. The ProMax simulation software, developed by Bryan Research & Engineering (BR&E), is widely used by the oil, gas, refining, and chemical industries for plant design and optimization. Capabilities of the ProMax simulation software include process areas such as amine sweetening, glycol dehydration, crude oil refining, and liquefied petroleum gas (LPG)/natural gas liquids (NGL) recovery and fractionation.

The objective of the simulation model is to provide the heat and energy balances necessary to perform the equipment sizing and cost estimate task. A detailed modeling approach was used in developing the MDEA model. This approach requires the identification of the major equipment within the unit and the construction of first principal separation models and/or detailed kinetic models. The MDEA model was developed based on the feed gas data and treated gas specifications provided by NREL and the process equipment design basis discussed in Section 3. In the ProMax simulation, the Amine Sweetening Electrolytic property package was used. The TSWEET Kinetics model was used for the absorber while the TSWEET Alternate Stripper model was used for the regenerator.

2.2 COST ESTIMATING APPROACH

2.2.1 Total Installed Equipment Cost Estimate

The total installed equipment cost was estimated using the equipment cost factoring approach. This approach is commonly used when detailed plant configuration of the process unit operation are available so that a major equipment list can be compiled and the size of each piece of equipment is determined. For this study, ICARUS was used to estimate the purchased (bare) equipment cost. Then, an appropriate installation factor was used to determine the field labor, piping, foundations, electrical, instrumentation, etc costs for each individual piece of equipment.

This method is well founded both theoretically and in practice. It has been in use for many years in petroleum and chemical process industries for plant cost estimating. This method relies on the observation that the total installed cost of major equipment can be reliably represented as a multiple of the equipment cost. For a given type of equipment, the multiplier (called the installed cost factor) can vary depending on the size of the piece of equipment, specific process design details, site location, and other factors.

2.2.2 Operating Costs

In general, the operating costs consist of variable operating costs and fixed operating costs. The variable operating costs of the MDEA unit include utilities and chemicals costs. This study assumes that steam and power purchase would not be required for the MDEA unit since the steam and power requirements would be supplied by the steam/power generation cycle, as shown in the current NREL design. (Refer to the Steam System and Power Generation of NREL design, PFD-P800-A602).^[2]

Generally, the fixed operating costs are determined for the entire plant complex, but not for the individual process units within the plant. Therefore, this study does not include the fixed operating costs for the MDEA unit.

Plant availability factor of 96%, which is the same basis as the current NREL design, is used for the operating cost estimates.

3.1 GENERAL DESIGN BASIS

3.1.1 Design Feed Gas

The feed gas to the MDEA unit, provided by NREL, is shown in Table 3-1.

Table 3-1 Feed Gas to the MDEA Unit

	Feed Gas to AGR
Total Flow, lbmol/hr	17,942
Temperature, °F	110
Pressure, psia	420
Compositions	mole%
H ₂	42.9
H ₂ O	0.3
CO	42.9
N ₂	0.8
CO ₂	11.4
H ₂ S	234 ppmv
NH ₃	82 ppmv
Methane (CH ₄)	1.4
n-Butane (C ₄ H ₁₀)	0.03
Ethane (C ₂ H ₆)	13 ppmv
Ethylene (C ₂ H ₄)	0.1
Acetylene (C ₂ H ₂)	0.0
Propane (C ₃ H ₈)	0.2
Pentane +	42 ppmv
Benzene (C ₆ H ₆)	3 ppmv
Tar (C ₁₀ H ₈)	0.4 ppmv

3.1.2 Design Product Gas

Approximately 153 MMSCFD of treated gas is produced from the MDEA unit. The treated gas is fed to the downstream alcohol synthesis reactor. The synthesis catalyst requires an H₂S concentration of up to 50 ppmv to maintain catalyst activity, and it can also tolerate a CO₂ concentration of up to 5 mol%. As agreed with NREL, acid gas concentrations of the treated gas should be within the following range:

H₂S: 10 to 50 ppmv
CO₂: 1 to 5 mol%

3.1.3 Amine Solutions

The two types of MDEA solutions evaluated in this study include:

- 50 wt% generic MDEA solution.
- Piperazine-activated MDEA solution to enhance CO₂ absorption.

3.1.4 Utilities

The utilities design basis for Task 2 was assumed to be similar to that used in the current NREL design. The major utilities requirements of the MDEA unit are cooling water, steam, and power. The following design basis was used in Task 2 study:

- Cooling water – supplied by the cooling water system, as shown on the current NREL design. CW is supplied at 90°F and returned at 110°F.
- Steam – 50 psig steam, produced by the steam/power generation cycle per the current MDEA design, is supplied to the MDEA unit.
- Electric power – supplied to the MDEA unit from the steam/power generation cycle as shown in the current MDEA design. Purchased power is not required.

3.2 MAJOR PROCESS EQUIPMENT DESIGN BASIS

Refer to Figure 4-1 for reference.

3.2.1 Absorber

- The lean solution inlet temperature is maintained at least 10°F higher than the temperature of the feed gas in order to avoid hydrocarbons condensation. Condensed hydrocarbons accumulated in the system may promote foaming.
- The rich acid gas loading of the absorber is not to exceed 0.40 mol acid gas/mol MDEA. For this application, the feed has a significantly higher ratio of CO₂ to H₂S, resulting in the rich amine solution being loaded mostly with CO₂. Since CO₂ is more corrosive than H₂S in aqueous solution, the rich acid gas loading is maintained at the mid-range of the recommended loading range rather than at the higher end. (Recommended rich acid gas loading range for MDEA: 0.2 - 0.55 mol acid gas/mol MDEA).
- The absorber is a tray column, designed for a jet flooding rate of 70% and a foaming factor of 0.8.
- Two minutes of surge time is provided between the HLL and LLL, based on rich amine flow rate.

- In the ProMax simulation, the TSWEET Kinetics absorber model was used to determine the number of theoretical stages and the MDEA circulation rate required to achieve the treated gas specifications. Tray efficiency of 20% was used to calculate the number of actual trays. Ideally, the actual operating data from a similar unit would be used to estimate the tray efficiency, but since such data is not available at present, tray efficiency was obtained from the open literature, which reported tray efficiency for gas absorption applications ranging from 10 - 30%.

3.2.2 Stripper

- The operating pressure of the stripper is set such that the reboiler bottom temperature does not exceed 255°F in order to minimize thermal degradation of the MDEA solution, which can lead to corrosion.
- The operating temperature of the stripper condenser is set at 120°F in order to maintain a 10°F approach temperature with the cooling water.
- Lean acid gas loading range: 0.004 to 0.01 mol acid gas/mol MDEA.
- Heating medium for the reboiler is 50 psig steam generated from the steam/power cycle.
- The stripper is a tray column, designed for a jet flooding rate of 85% and a foaming factor of 0.85.
- In the ProMax simulation, the TSWEET Alternate Stripper model was used to determine the number of theoretical stages and the reboiler duty required to achieve the lean acid gas loading that is within the range specified above. Tray efficiency of 40%, obtained from literature, was used to calculate the number of actual trays.

3.2.3 Lean/Rich Exchanger

- The exchanger's fluid velocities are kept at a maximum of 4 ft/s to minimize corrosion.
- Minimum end approach temperature of at least 20°F (lean amine temperature out – rich amine temperature in).

3.2.4 Lean Amine Treating and Cooling

- The lean amine solution from the stripper is cooled by heat exchanged with the rich solution in the Lean/Rich Exchanger. The lean solution is further cooled to 120°F by water cooling in the Lean Solution Cooler, which has a minimum approach temperature of 10°F.

- A filtration unit is provided for solution maintenance. The presence of particulates in the amine solution tends to promote solution foaming while degradation products can contribute to foaming and corrosion. The filtration unit is a package unit, consisting of a 5-micron cotton pre-filter to remove particulates, followed by an activated carbon bed to remove degradation products, and ends with a 5-micron cotton post-filter to remove any carry-over carbon particles to minimize solution foaming tendencies. Approximately 10% of the lean amine solution is continuously filtered.
- Since the acid gases to the MDEA unit are primarily CO_2 and H_2S , and their reactions with MDEA form regenerable compounds that can be regenerated in the stripper, a reclaimer unit is not provided in this design.
- An amine sump is provided to prepare make-up solutions and to collect and recover amine from drainage lines.

3.2.5 Materials of Construction

- Carbon steel is used, except in portions of the plant that are exposed to wet CO_2 or $\text{CO}_2/\text{H}_2\text{S}$ evolution, in which stainless steel is used. All equipment is stress relieved.

3.3 OTHER CONSIDERATIONS

3.3.1 Impurities in Feed Stream

- Ammonia – As shown in Table 3-1, the feed gas to the MDEA unit contains a small quantity of ammonia. Due to the high solubility of ammonia in water, virtually all of the ammonia in the feed gas stream is absorbed by the amine solution in the absorber. Ammonia is then released along with the H_2S and CO_2 in the stripper. In the stripper condenser, it is condensed with the water and is returned to the column as reflux. Overtime, ammonia builds up in the stripper overhead system and contributes to corrosion. Additionally, the presence of ammonia also impacts the energy requirements of the stripper condenser and reboiler. The condensation of ammonia is highly exothermic while the vaporization of ammonia requires considerable amount of heat, consequently resulting in increased condenser and reboiler duties. Ammonia buildup can be minimized by purging a portion of the reflux water.
- HCl – although the feed gas in this study does not contain HCl, but according to NREL, some biomass-derived gases may contain small quantities of HCl. HCl reacts with the amine to form heat-stable, degradation compounds that cannot be regenerated in the stripper. Generally in this situation, soda ash is added into the solution to neutralize the heat-stable compounds. Once concentration of these compounds reaches about 4 wt%, then the MDEA solution is reclaimed^[3].

3.3.2 Emissions of Absorbed Product Gases

The feed gas to the MDEA unit contains high concentrations of hydrogen, CO, and small quantities of hydrocarbons, primarily methane. These compounds are absorbed to some extent in the absorber. The absorption of these compounds has an environment impact since these gases, which exit the MDEA unit with the acid gas stream, would be vented with the CO₂ stream from the LO-CAT sulfur recovery unit (Figure ES-1). (CO is a criteria pollutant and methane is a greenhouse gas).

According to the EPA, the allowable concentrations of CO and methane are dependent on the specific application and plant location. Since a site has not yet been selected for the NREL thermochemical ethanol process, and the acceptable emissions level cannot be determined at this time, the MDEA unit is designed to minimize the emissions level of CO and methane by depressuring the rich amine solution in order to recover the dissolved gases.

4.1 PROCESS DESCRIPTION

Figure 4-1 illustrates a simplified process flow diagram of the MDEA unit. Two types of MDEA solutions are considered for the process: a generic 50 wt% MDEA solution and a piperazine activated MDEA solution. Descriptions of the process and the activated MDEA solution are provided below.

Amine Absorption

The sour gas enters the bottom of the absorber at 110°F and 420 psia. The lean MDEA solvent enters the top of the absorber at 120°F. As the solvent contacts the gas stream, the acid gases (H_2S and CO_2) react with the MDEA. As a result, the H_2S and CO_2 in the feed gas are transferred to the solvent. Additionally, small amounts of CO, methane, and hydrogen, and virtually all of the NH_3 in the feed gas are also absorbed into the MDEA solution. Makeup water is added to the water trays at the top of the column.

The treated gas exits at the top of the absorber, where a demister pad is installed near the overhead gas outlet to trap the entrained MDEA solvent. A knockout drum is provided for the treated gas to collect residual solvent carryover. If necessary, the treated gas is injected with a small amount of dimethyl disulfide (DMDS) to control the H_2S content in order to maintain the catalyst activity of the downstream alcohol synthesis reactor. DMDS is commonly used as a sulfiding reagent in industrial applications to control catalyst activity. In this design, DMDS is pumped and injected into the clean gas stream after the gas is compressed and preheated to the operating conditions of the alcohol synthesis reactor. Injection into a hot gas line is preferable so that the liquid DMDS can be vaporized.

Rich Solution Flashing

The rich amine solution from the absorber bottom is depressured through the Flash Drum to about 50 psia to recover the CO, methane, and hydrogen dissolved in the MDEA solution. (The ammonia remains in the rich solution). Depressuring the rich solution to recover the dissolved gases helps to minimize their emissions into the atmosphere as they would be vented along with the CO_2 stream from the LO-CAT sulfur recovery unit.

The flashed gas stream is to be combined with the unreacted syngas stream (operating at 34 psia) from the alcohol synthesis area (NREL design, PFD-P800-A402, stream 426)^[2] and fed to the Catalyst Regenerator (R-301A) as purge gas. In the Catalyst Regenerator, the CO and methane compounds are destroyed by incineration.

Another option to handle the flashed gas would be to re-compress and recycle the gas to the absorber. However, because the flashed gas stream is fairly small—the CO, H_2 , and methane contents in the flashed gas are equivalent to just 0.1%, or less, of the respective feed gas

components—it would not justify the added capital cost and complexity of the recycle loop. For this reason, the flashed gas recycle option is not considered for the MDEA design.

Amine Stripping, Treating & Cooling

The rich solvent from the flash drum is preheated before entering the stripper by exchanging heat with the lean MDEA stream from the stripper. The Lean/Rich Exchanger is a shell and tube exchanger, with the rich solvent on the tube side. In the stripper, as the rich MDEA solution travels down the column, the H₂S and CO₂ are stripped from the solution by the stripping steam generated in the kettle reboiler.

The stripped acid gases exit at the top of the stripper and enter the condenser where the water vapor is condensed and returned to the column as reflux. A portion of the reflux water is purged in order to minimize ammonia buildup in the stripper. The purged stream is sent to the waste water treatment facility. The acid gas from the reflux drum overhead is sent to the LO-CAT sulfur recovery unit for processing.

Lean MDEA solution from the bottom of the stripper, after cooling by heat exchange with the rich solution, is sent to the MDEA Surge Tank. The lean solution is then pumped to about 450 pisa and cooled to 120°F before it enters the absorber.

A portion of the lean solution, approximately 10%, is continuously filtered through the MDEA Pre-Filter to remove solids which tend to promote solution foaming as well as plugging of downstream carbon filter. From the MDEA Pre-Filter, the lean solution passes through the MDEA Carbon Bed to remove degradation products which tend to promote foaming and corrosion. Carbon filter effluent then passes through the MDEA Post-Filter to remove any carry-over carbon particle.

A sump is provided for preparation of makeup solutions and for collection of drainage to recover amine. All amine containing lines and equipment are to drain to the amine sump to minimize amine losses.

4.2 PIPERAZINE-ACTIVATED MDEA SOLUTION

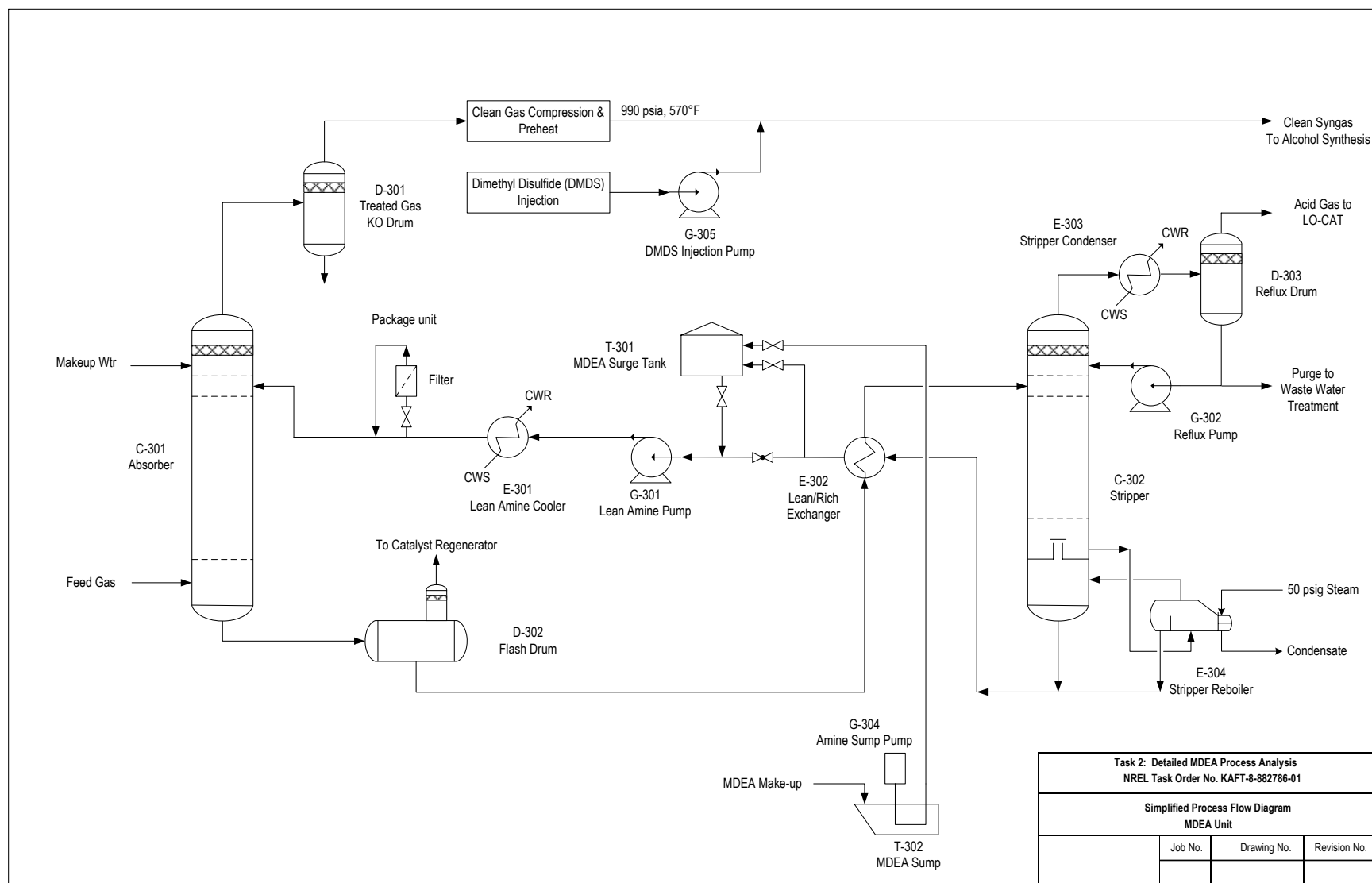
The rate of CO₂ absorption in MDEA solution is considerably lower compared to that of H₂S absorption due to the low reaction rate of MDEA with CO₂. The CO₂ absorption rate can be significantly enhanced by the addition of promoters, such as piperazine. For many years, piperazine-activated MDEA has been successfully used in natural gas, ammonia, and syngas plants for high capacity CO₂ removal. The use of piperazine-activated MDEA was patented by BASF, until 2002, under the name aMDEA. At present, MDEA with piperazine promoter is offered by most solution vendors under various trade names.

The advantages of piperazine are its high reactivity towards CO₂ and its high carrying capacity for CO₂. According to studies conducted by Bishnoi and Rochelle^[4], the addition of piperazine (5 wt%) to 45 wt% MDEA increases the CO₂ absorption rate by approximately two orders of

magnitude at low loading and one order of magnitude at moderate loading compared to 50 wt% MDEA. These characteristics make piperazine-activated solution suitable for applications with appreciably high CO₂ concentration relative to H₂S.

Typically, the piperazine concentration in the MDEA solution is specified by the solution vendors based on the desired removal target. BASF's aMDEA process uses a 2.5-4.5 M (30-54 wt%) MDEA solution containing up to 0.8 M (7 wt%) piperazine^[3]. For this study, the amine solution evaluated is a mixture of 50 wt% MDEA and 2 wt% piperazine. Higher piperazine concentrations were also evaluated, and the simulation results indicated that piperazine addition of about 2 wt% would be sufficient to achieve the required acid gas removal target for the NREL design.

Figure 4-1 Simplified MDEA Process Flow Diagram



5.1 OVERVIEW

In this study, a detailed analysis of the MDEA acid gas removal unit was performed for the NREL thermochemical ethanol synthesis process. The detailed analysis entails the development of an MDEA process model to obtain the heat and energy balance of the MDEA unit and the cost estimation of the unit. The MDEA solutions evaluated are generic MDEA (Case 1) and activated MDEA (Case 2) solutions. The following sections present the analysis results of the two cases.

Additionally, a sensitivity analysis was also performed to determine the impact of ammonia and of varying acid gas concentrations in the feed gas on the utilities requirements of the unit.

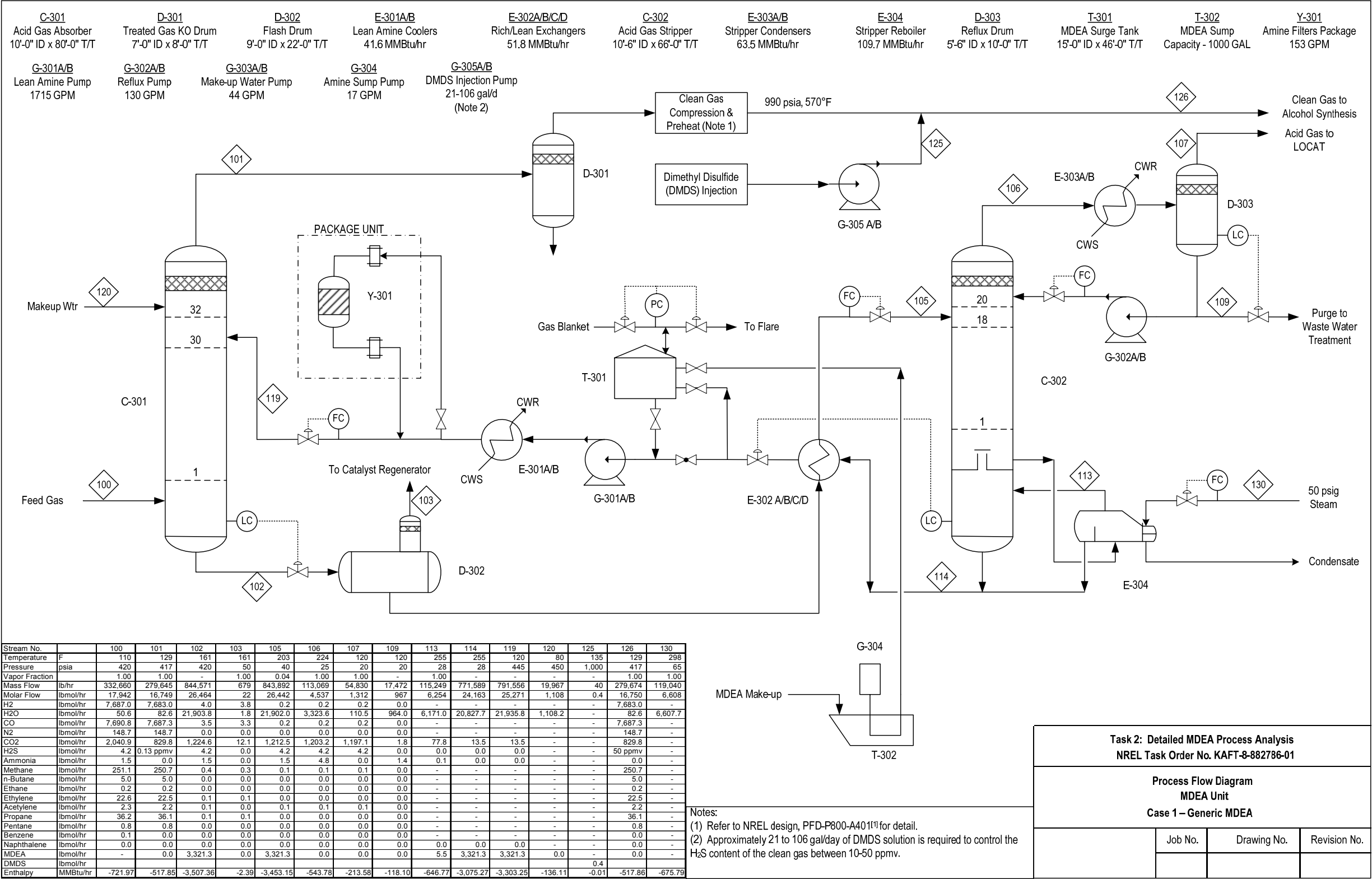
5.2 CASE 1 – GENERIC MDEA**5.2.1 Discussion of Results**

Figure 5-1 illustrates the MDEA unit utilizing a generic 50 wt% MDEA solution to treat the NREL biomass-derived syngas. The unit's material and energy balance are also shown on Figure 5-1. In this case, the absorber with 32 total actual trays—30 trays for acid gas absorption and 2 trays for makeup water addition—and an amine circulation rate of approximately 1533 gpm are required to treat the sour feed gas containing 234 ppmv H₂S and 11.4 mol% CO₂. The achieved purity of the clean gas is 0.13 ppmv H₂S and 4.95 mol% CO₂. Due to the selectivity of MDEA for H₂S, the amount of H₂S removal has to be higher than necessary in order to meet the CO₂ specification in the clean gas. As a result, the H₂S content in the clean gas is lower than the specified 10 – 50 ppmv required to maintain the alcohol synthesis catalyst activity. To increase the H₂S content of the clean gas, DMDS solution is injected into the clean gas after the gas is compressed and preheated to the operating conditions of the alcohol synthesis reactor. The cost and the amount of DMDS required to achieve various levels of H₂S content in the clean gas are shown in the operating cost section.

The rich amine solution entering the amine stripper has an acid gas loading of 0.37 mol/mol MDEA. The stripper unit, which has 20 total actual trays plus 1 chimney tray for reboiler draw, can achieve a lean loading of 0.004 mol acid gas/mol MDEA by utilizing 119,000 lb/hr of 50 psig steam. For this unit, the heat duty per lb of acid gas removed is 2,053 Btu/lb.

From the reflux drum, approximately 30% of the reflux water, or 35 gpm, is purged in order to minimize ammonia buildup in the amine stripper. The water balance of the unit is maintained by the addition of about 40 gpm of make-up water to the absorber.

Figure 5-1 Case 1 - MDEA Process Flow Diagram



5.2.1.1 Utilities Requirements

Table 5-1 summarizes the overall utilities requirements of the MDEA unit. Detailed utilities requirements of individual equipment are provided in Appendix A. The unit requires approximately 119,000 lb/hr of 50 psig steam for the stripper reboiler, 10,497 gpm of cooling water circulation for the cooling and/or condensing of the stripper overhead and the lean amine solution, and 569 kW of electric power, mainly for the pumping of the lean solution to the absorber. Additionally, 40 gpm of make-up water to the absorber is also required.

As noted in the design basis in Section 2, it is assumed that the steam and power requirements of the MDEA unit are supplied by the steam/power generation cycle as shown in the current NREL design (PFD-P800-A602)^[2]. Thus the steam/power generation cycle design should be revised based on the utilities requirements provided from this study.

Table 5-1 Case 1 – Overall Utilities Requirements

Steam (50 psig), klb/hr	119
Electric Power, kW	569
Cooling Water Circulation, gpm	10,497
Make-up Water, gpm	40

5.2.1.2 Equipment Cost Estimates

The detailed equipment list, including equipment sizes, and the equipment cost estimates for the MDEA unit are shown in Appendix A. The equipment cost was estimated using ICARUS based on 2nd quarter 2009 dollars. For this case, the bare equipment cost is 4.4 million dollars. The installation factor is calculated to be 2.61 and the total installed equipment cost is 11.6 million dollars.

5.2.1.3 Variable Operating Costs

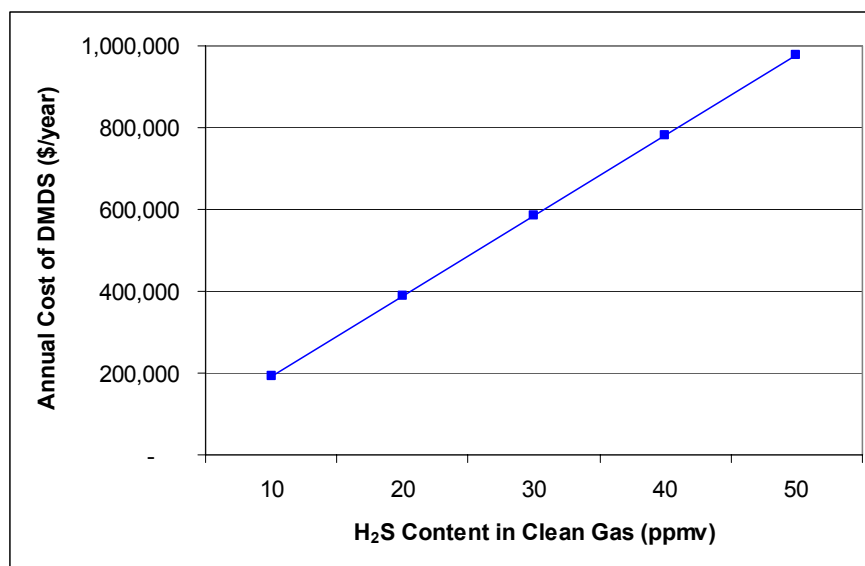
The variable operating costs of the MDEA unit, which include the utilities and chemicals costs, are shown in Table 5-2. The variable operating costs estimates are based on 96% plant availability. The MDEA make-up requirement is based on the amine loss of approximately 0.91 lb MDEA per MMSCF of treated gas. Amine loss includes losses from entrainment and vaporization.

Table 5-2 Case 1 – Variable Operating Cost Estimates

Utilities & Chemicals	Unit Cost	Consumption		Cost	
		Initial	per Day	Initial	Annual
Water (1000 gal)	1.03 \$/1000gal	-	57	-	\$20,662
MDEA Solution (gal)	8.38 \$/gal	25,408	16	\$212,923	\$46,929
DMDS Solution (gal), (min)	26.25 \$/gal	-	21	-	\$193,338
DMDS Solution (gal), (max)	26.25 \$/gal	-	106	-	\$977,152
Total Variable Operating Costs (min)					\$260,930
Total Variable Operating Costs (max)					\$1,044,744

The DMDS solution consumptions shown on Table 5-2 are the quantities required per day in order to increase the H₂S content of the clean gas from 0.13 ppmv to 10 ppmv (minimum requirement) and to 50 ppmv (maximum requirement), respectively. As Figure 5-2 shows, the annual operating cost of sulfur injection can increase considerably with increasing H₂S content of the clean gas. Therefore, consultation with the catalyst vendor is recommended to obtain the optimal H₂S content in the clean gas such that the catalyst activity can be maintained while minimizing the operating cost.

Figure 5-2 Case 1 – Estimated Annual Cost of Sulfur Injection



5.2.2 Summary of Results

Table 5-3 summarizes the results of Case 1 discussed above.

Table 5-3 Case 1 – Summary of Results

<u>Design Feed Rates</u>		Case 1
Feed Gas	MMSCFD	163
Feed Gas H ₂ S Concentration	ppmv	234
Feed Gas CO ₂ Concentration	mol %	11
Amine Type		MDEA
Amine Concentration	wt%	50
Amine Circulation rate	gpm	1,534
Steam Consumption	klb/h	119
Power Consumption	kW	569
Make-up Water	gpm	40
DMDS Consumption (Note 1)	gal/d	21-106
<u>Design Product Rates</u>		
Treated Gas	MMSCFD	153
Treated Gas H ₂ S Concentration	ppmv	0.13
Treated Gas CO ₂ Concentration	mol %	4.95
Heat Duty per lb Acid Gas Removed	Btu/lb	2,053
<u>Capital & Operating Costs</u>		
Total Installed Equipment Cost, (2Q09)	million \$	11.6
Annual Operating Costs (min) (Note 2)	thousand \$	260.9
Annual Operating Costs (max) (Note 2)	thousand \$	1,044.7

Notes:

- (1) The range of DMDS injection shown represents the minimum and maximum levels of sulfur injection required in order to maintain the H₂S content of the clean gas between 10 – 50 ppmv.
- (2) The minimum and maximum operating costs shown reflect the level of DMDS consumption.

5.3 CASE 2 – ACTIVATED MDEA

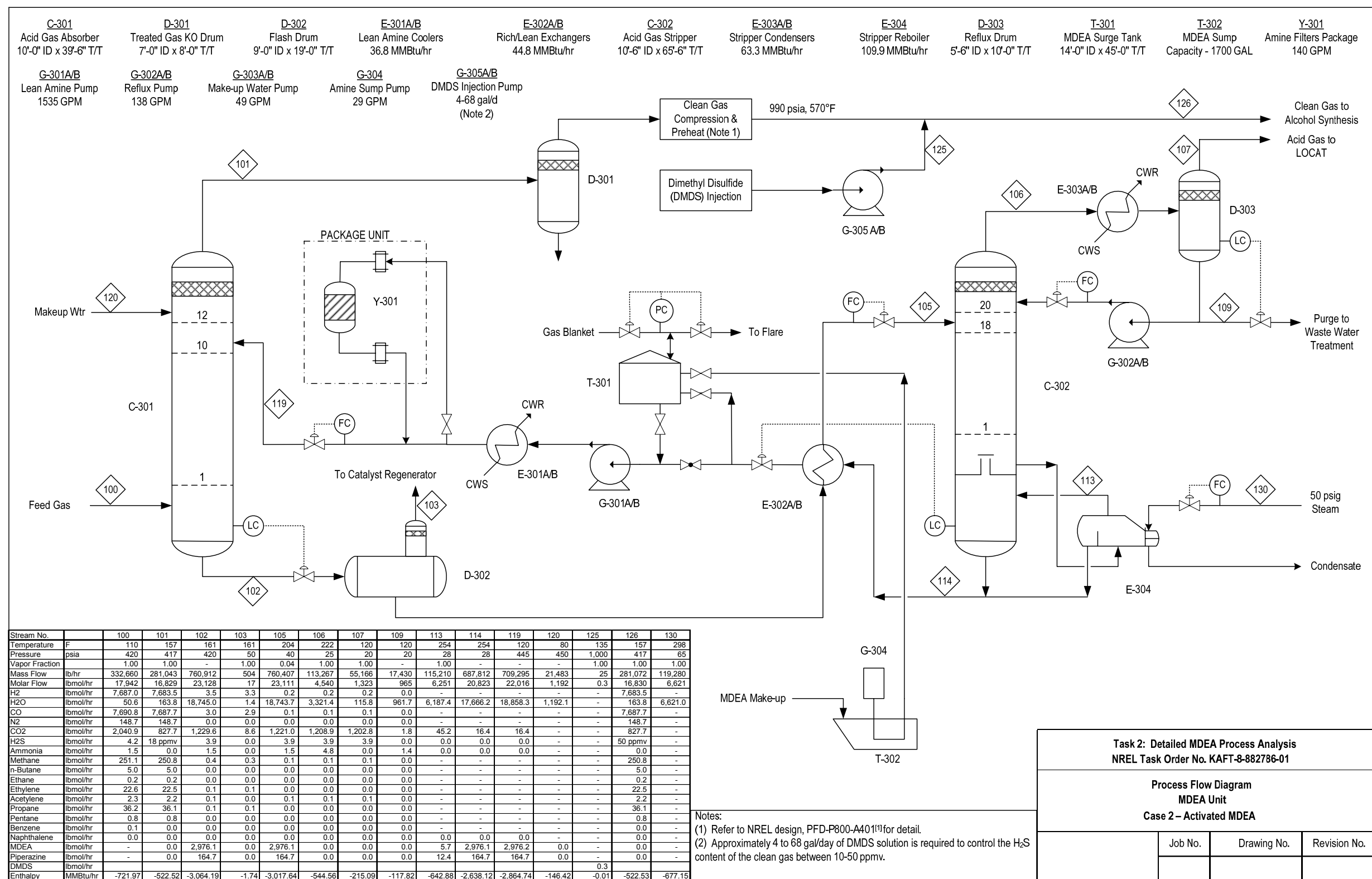
5.3.1 Discussion of Results

Figure 5-3 illustrates the MDEA unit utilizing a piperazine-activated MDEA solution (50 wt% MDEA and 2 wt% piperazine) to treat the NREL biomass-derived syngas. The unit's material and energy balance are also shown on Figure 5-2. In this case, the absorber with 12 total actual trays—10 trays for acid gas absorption and 2 trays for makeup water addition—and an amine circulation rate of approximately 1406 gpm are required to treat the sour feed gas containing 234 ppmv H₂S and 11.4 mol% CO₂. The achieved purity of the clean gas is 18 ppmv H₂S and 4.92 mol% CO₂. In this case, the H₂S content meets minimum concentration required for alcohol synthesis. If a higher H₂S concentration in the treated gas is desirable, DMDS injection similar to Case 1 can be utilized.

As discussed in Section 4.2, piperazine can significantly increase the rate of CO₂ absorption into the amine solution. As more CO₂ is absorbed by the solution, its capacity for H₂S absorption decreases. Consequently, less H₂S is removed, resulting in a higher H₂S content in the clean gas compared to Case 1. Additionally, due to the enhanced CO₂ absorption capability of the amine solution, less amine circulation rate and fewer absorber stages are required, as compared to Case 1, to achieve the treated gas specifications. The results indicated that this case requires 10% less circulation rate and 20 fewer absorption stages compared to Case 1.

The rich amine solution entering the amine stripper has an acid gas loading of 0.39 mol/mol MDEA. The stripper unit, which has 20 total actual trays plus 1 chimney tray for reboiler draw, can achieve a lean loading of 0.005 mol acid gas/mol MDEA by utilizing 119,000 lb/hr of 50 psig steam. From the reflux drum, approximately 30% of the reflux water, or 35 gpm, is purged in order to minimize ammonia buildup in the amine stripper. The water balance of the unit is maintained by the addition of about 43 gpm of make-up water to the absorber.

Figure 5-3 Case 2 – Activated MDEA Process Flow Diagram



5.3.1.1 Case 2 Utilities Requirements

Table 5-4 summarizes the utilities requirements of the MDEA unit. The unit requires approximately 119,000 lb/hr of 50 psig steam for the stripper reboiler, 9,996 gpm of cooling water circulation for the cooling and/or condensing of the stripper overhead and the lean amine solution, and 497 kW of electric power, mainly for the pumping of the lean solution to the absorber. Additionally, 43 gpm of make-up water to the absorber is also required.

Table 5-4 Case 2 – Overall Utilities Requirements

Steam (50 psig), klb/hr	119
Electric Power, kW	497
Cooling Water Circulation, gpm	9,996
Make-up Water, gpm	43

5.3.1.2 Case 2 Equipment Cost Estimates

The detailed equipment list, including equipment sizes, and the equipment cost estimates for the MDEA unit are shown in Appendix B. The equipment cost was estimated using ICARUS based on 2nd quarter 2009 dollars. For this case, the bare equipment cost is 3.7 million dollars. The installation factor is calculated to be 2.61, and the total installed equipment cost is 9.7 million dollars.

5.3.1.3 Case 2 Variable Operating Cost

The variable operating costs of the MDEA unit, which include the utilities and chemicals costs, are shown in Table 5-5. The variable operating costs estimates are based on 96% plant availability. The MDEA make-up requirement is based on the amine loss of approximately 1.5 lb MDEA per MMSCF of treated gas. Amine loss includes losses from entrainment and vaporization.

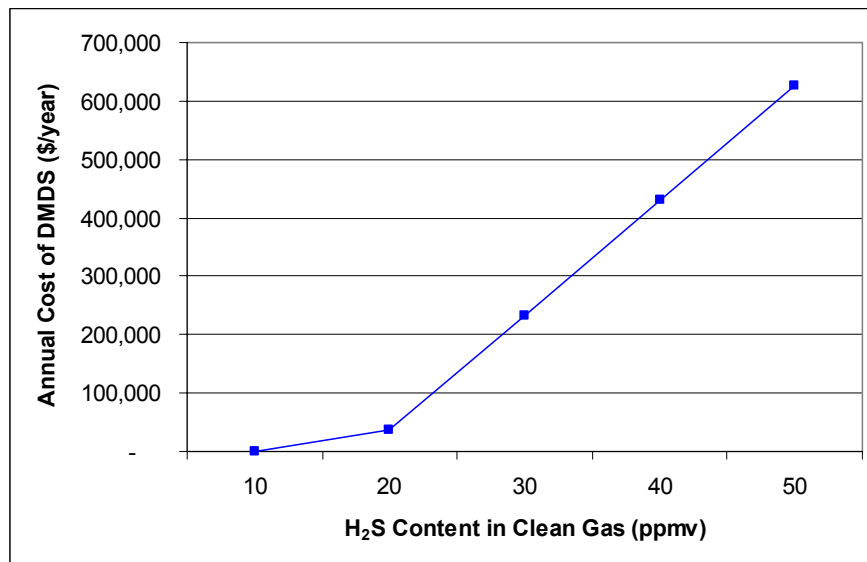
Table 5-5 Case 2 – Variable Operating Cost Estimates

Utilities & Chemicals	Unit Cost	Consumption		Cost	
		Initial	per Day	Initial	Annual
Water (1000 gal)	1.03 \$/1000gal	-	62	-	\$22,299
Activated MDEA Solution (gal)	9.22 \$/gal	21,248	27	\$195,864	\$87,384
DMDS Solution (gal), (min)	26.25 \$/gal	-	4	-	\$36,263
DMDS Solution (gal), (max)	26.25 \$/gal	-	68	-	\$626,946
Total Variable Operating Costs (min)					\$145,946
Total Variable Operating Costs (max)					\$736,629

For this case, the clean gas has an H₂S concentration of approximately 18 ppmv, which meets the minimum requirement needed to maintain the alcohol synthesis catalyst activity. Therefore, DMDS injection may not be necessary, depending on the catalyst vendor's recommendation.

Figure 5-4 shows the incremental annual cost of DMDS injection to increase the H_2S concentration in the clean gas up to 50 ppmv, should this option be desirable.

Figure 5-4 Case 2 – Estimated Annual Cost of Sulfur Injection



5.3.2 Summary of Results

Table 5-6 summarizes the results of Case 2 discussed above.

Table 5-6 Case 2 – Summary of Results

<u>Design Feed Rates</u>		Case 2
Feed Gas	MMSCFD	163
Feed Gas H ₂ S Concentration	ppmv	234
Feed Gas CO ₂ Concentration	mol %	11
Amine Type		Activated MDEA
Amine Concentration (MDEA/PZ)	wt%	50/2
Amine Circulation rate	gpm	1,374
Steam Consumption	klb/h	119
Power Consumption	kW	497
Make-up Water	gpm	43
DMDS Consumption (Note 1)	gal/d	4-68
<u>Design Product Rates</u>		
Treated Gas	MMSCFD	153
Treated Gas H ₂ S Concentration	ppmv	18
Treated Gas CO ₂ Concentration	mol %	4.92
Heat Duty per lb Acid Gas Removed	Btu/lb	2,053
<u>Capital & Operating Costs</u>		
Total Installed Equipment Cost, (2Q09)	million \$	9.7
Annual Operating Costs (min) (Note 2)	thousand \$	145.9
Annual Operating Costs (max) (Note 2)	thousand \$	736.6

Note:

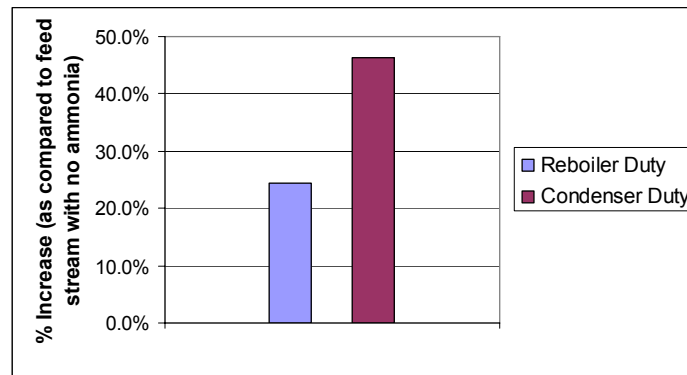
- (1) The range of DMDS injection shown represents the minimum and maximum levels of sulfur injection required in order to maintain the H₂S content of the clean gas between 10 – 50 ppmv.
- (2) The minimum and maximum operating costs shown reflect the level of DMDS consumption

5.4 SENSITIVITY ANALYSIS

The sensitivity analysis examines the impact of ammonia and of varying acid gas concentrations in the feed stream on the utilities requirements of the MDEA unit.

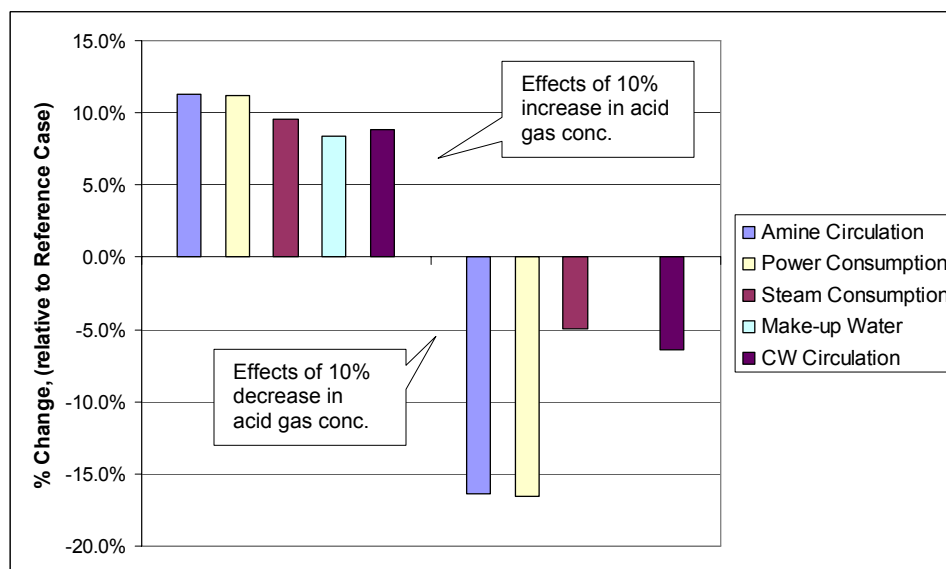
As noted, the presence of ammonia in the feed gas can significantly increase the duties of the stripper unit's condenser and reboiler because the condensation of ammonia is highly exothermic and the vaporization of ammonia requires considerable amount of heat. This effect is illustrated in Figure 5-5, which shows an increase in duties of about 25% in the reboiler and 45% in the condenser, compared to the feed gas with no ammonia present. As the impact of ammonia on the unit's utilities requirements is substantial, coupled with the potential corrosion problems due to ammonia buildup in the stripper overhead system, the removal of ammonia upstream of the AGR unit is critical to minimize operating problems as well as operating costs.

Figure 5-5 Effects of Ammonia on Utilities Requirements



The MDEA unit utilizing a generic MDEA solution (Case 1) was used as the reference case for the sensitivity analysis to determine the impact of varying acid gas concentrations in the feed stream on the utilities requirements of the unit. This analysis assumes that the volumetric flow rate of the feed gas is the same as the reference case, and only the H_2S and CO_2 concentrations are varied by $\pm 10\%$. Figure 5-6 illustrates the percentage change in utilities requirements, relative to the reference case, as the H_2S and CO_2 concentrations in the feed gas are varied. The analysis results show that when the acid gas concentrations are increased by 10%, the utilities requirements of the unit increase between 9-11%. When the acid gas concentrations are decreased by 10%, the impact on power consumption, with reduction of about 16%, is considerable; however, the impact on steam and cooling water circulation requirements are less pronounced. This is most likely due the effect of ammonia on the reboiler and condenser duties, as shown above. The results show no change in make-up water requirement when the acid gas concentration decreases.

Figure 5-6 Effects of Varying Acid Gas Concentrations on Utilities Requirements



This study conducted a detailed analysis of the MDEA system remove acid gases from the NREL biomass-derived syngas. The MDEA system is designed to treat approximately 163 MMSCFD of syngas containing 234 ppmv H₂S and 11.4 mol% CO₂. The required purity of the treated gas, which is dictated by the sulfur requirement and CO₂ tolerance of the alcohol synthesis catalyst, are 10 – 50 ppmv H₂S and 1 - 5 mol% CO₂. This study evaluated two types of solution the MDEA system: a generic 50 wt% MDEA solution (Case 1) and an activated MDEA solution consisting of a mixture of 50 wt% MDEA and 2% piperazine (Case 2).

The analysis showed that the presence of ammonia in the feed stream has a major impact on the utilities requirements of the MDEA unit. Moreover, the presence of ammonia eventually leads to buildup in the stripper overhead system and contributes to corrosion. For these reasons, the removal of ammonia upstream of the AGR unit is critical to minimize operating problems as well as operating costs.

The analysis results indicated that for the NREL thermochemical ethanol synthesis application, in which the syngas to be treated in the MDEA unit has appreciably higher concentration of CO₂ relative to H₂S, the use of a piperazine promoter in the MDEA solution to enhance the rate of CO₂ absorption is very favorable. Due to the enhanced CO₂ absorption capability of the amine solution, the MDEA unit requires less amine circulation rate and fewer absorber stages than one using a generic 50 wt% solution (Case 1). Consequently, due to the smaller plant size, the total installed equipment cost is approximately 16% lower compared to Case1. Additionally, the operating costs of the MDEA unit in Case 2 are 30-45% lower compared to Case 1, primarily due to lower DMDS requirement for controlling the H₂S content of the clean gas at appropriate levels in order to maintain the alcohol synthesis catalyst activity. Thus, for the NREL design, the MDEA system utilizing an activated MDEA solution has more economics advantages over the one utilizing a generic MDEA solution.

References

1. Nexant Inc. *Task 1: Acid Gas Removal Technology Survey and Screening for Thermochemical Ethanol Synthesis*. Subcontract Report NREL/KAFT-8-882786-01. March 2009.
2. Phillips, S., Aden, A., Jechura, J., Dayton, D., and Eggeman, T., "Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass," NREL Report No. TP-510-41168, April 2007.
3. Kohl, A. L., and Nielsen, R. B., *Gas Purification*, 5th ed., Gulf Publishing, Houston, TX, 1997.
4. Bishnoi, S. and G. T. Rochelle, "Absorption of Carbon Dioxide in Aqueous Piperazine/Methyldiethanolamine," *AIChE Journal*, Vol. 48, No. 12, December 2002, pp. 2788 - 2799.

Table A-1 Case 1 – Detailed Utilities Requirements

Item No	Item Name	Load BHP		Elect. Power	Steam 1000 lbs/hr	Water Requirement, 1000 lbs/hr		Cooling Water	
		Norm.	Max.	KW	50 psig / 298 F	Return Cond. 50 Psig / 298 F	Make-up	CW, MMbtu/hr	C.W. circ. GPM
C-301	Acid Gas Absorber						20.0		
E-301A/B	Lean Amine Cooler							41.6	4,155
E-303 A/B	Stripper Condenser							63.5	6,342
E-304	Stripper Reboiler				119.0	(119.0)			
G-301 A/B	Lean Amine Pump	663.6		549.8					
G-302 A/B	Reflux Pump	6.7		5.2					
G-303 A/B	Makeup Water Pump	16.9		14.2					
G-304	Amine Sump Pump (Note 2)	0.5		0.4					
G-305 A/B	DMDS Injection Pump	0.1		0.1					
	TOTAL	687		569	119.0	(119.0)	20.0	105.1	10,497
NOTES: (1) Negative numbers (xxx) are productions while positive numbers are consumptions. (2) Numbers shown are intermittent consumptions and are NOT included in NORMAL total.									

Table A-2 Case 1 - Equipment List

Columns	Item Name	Quantity	Type	Dimensions		Design		Mat'l of Construction (M.O.C)		Comments
				I.D (FT)	T-T (FT)	Press. (PSIG)	Temp (°F)	Shell	Internals	
C-301	Acid Gas Absorber	1	Vertical	10.0	80.0	450	220	CS & SR		SR - Stress Relief
	Valve Trays	32	Internal Devices	10.0	N/A				304 SS	
	Liquid Distributors	2	Internal Devices	10.0	N/A				304 SS	
	Demister Pads	1	Internal Devices	10.0	N/A				304 SS	
C-302	Acid Gas Stripper	1	Vertical	10.5	66.0	50	310	CS/304 SS Clad		
	Valve Trays	20	Internal Devices	10.5	N/A				304 SS	
	Chimney Trays	1	Internal Devices	10.5	N/A				304 SS	
	Liquid Distributors	2	Internal Devices	10.5	N/A				304 SS	
	Demister Pads	1	Internal Devices	10.5	N/A				304 SS	
Vessels & Tanks	Item Name	Quantity	Type	Dimensions		Design		M.O.C	Internals	Comments
				I.D (FT)	T-T (FT)	Press. (PSIG)	Temp (°F)			
D-301	Treated Gas Knockout Drum	1	Vertical	7.0	8.0	440	180	CS	Demister pad	
D-302	Flash Drum	1	Horizontal	9.0	22.0	50	210	CS & SR		
	Flash Drum Top Column	1	Vertical	3.0	6.0	50	210	CS & SR	Demister pad	
D-303	Reflux Drum	1	Vertical	5.5	10.0	20	170	CS & SR	Demister pad	
T-301	MDEA Surge Tank	1	Cone Roof	15.0	46.0	ATM	310	CS		
T-302	MDEA Sump	1	In Ground					Concrete		Capacity: 1000 gal
Exchangers	Item Name	Quantity	Type	Total Duty	Tot. Bare Tube Area	Design		M.O.C		
				MMBTU/HR	SQ FT	Press. (PSIG)	Temp (°F)			
E-301A/B	Lean Amine Cooler	2	S & T	41.59	7,660	S 80 T 480	240 240	CS & SR CS & SR		
E-302 A/B/C/D	Lean/Rich Exchangers	4	S & T	51.83	30,400	S 30 T 50	310 310	304 SS 304 SS		
E-303 A/B	Stripper Condenser	2	S & T	63.48	8,288	S 30 T 80	280 280	304 SS 304 SS		
E-304	Stripper Reboiler	1	Kettle	109.67	14,260	S 30 T 70	350 350	304 SS 304 SS		
Pumps	Item Name	Quantity	Type	Design Capacity			Power		M.O.C	
				Flow (GPM)	Inlet PSIG	Delta PSI	Pump BHP	Driver HP	Casing	Impeller
G-301 A/B	Lean Amine Pump	2	Cent	1,715	3.6	432	664	737	CS	316 SS 2x100%
G-302 A/B	Reflux Pump	2	Cent	130	5.6	14	7	7	CS	316 SS 2x100%
G-303 A/B	Makeup Water Pump	2	Cent	44	ATM	435	17	19	CS	CS 2x100%
G-304	Amine Sump Pump	1	Vert. Cent	17	ATM	10	0.5	1	CS	CS 1x100%. No Spare.
G-305 A/B	DMDS Injection Pump	2	Meter	0.08	43	942	0.07	0.07	CS	CS 2x100%
Miscellaneous	Item Name	Quantity		Design Capacity			Design		M.O.C	
							Press. (PSIG)	Temp (°F)		
Y-301	Filters (Carbon + Pre & Post Filters)	1	Package	153.40	GPM of lean MDEA		50	310	CS & SR	5 micron pre & post filters.

Table A-3 Case 1 - Equipment Cost Estimates

DESCRIPTION	QTY	UNIT	COSTS IN US\$ (2Q09)				
			EQUIPMENT	BULK	LABOR	SUBCONTR/ OTHER	TOTAL
<u>PROCESS EQUIPMENT & DUCTWORK</u>							
PUMPS & DRIVERS	10	EA	503,200		37,000		540,200
HEAT EXCHANGERS	9	EA	2,017,591		23,000		2,040,591
TANKS & STORAGE FACILITIES	1	EA	53,500		2,000		55,500
MATL HANDLING & PROCESSING - FILTERS	1	EA	134,500		5,000		139,500
COLUMNS & VESSELS (INCL HEAVY/OVERSIZE TRANSPORT)	5	EA	1,401,770		66,500		1,468,270
FREIGHT (EQUIPMENT EXCEPT HEAVY/OVERSIZE TRANSPORT)	5	%	<u>205,500</u>				<u>205,500</u>
TOTAL PROCESS EQUIPMENT & DUCTWORK	26	EA	4,316,061		133,500		4,449,561
INSTRUMENTS				647,400	252,500		899,900
PIPING				1,294,800	1,431,000		2,725,800
STEELWORK				259,000	185,000		444,000
INSULATION						431,600	431,600
ELECTRICAL				647,400	799,500		1,446,900
CONCRETE				215,800	308,500		524,300
BUILDING							
SITWORK				215,800	449,000		664,800
PAINTING						43,200	43,200
TOTAL DIRECT COSTS				3,280,200	3,425,500	474,800	7,180,500
TOTAL INSTALLED EQUIPMENT COSTS			4,316,061	3,280,200	3,559,000	474,800	11,630,061

Table B-1 Case 2 – Detailed Utilities Requirements

Item No	Item Name	Load BHP		Elect. Power	Steam 1000 lbs/hr	Water Requirement, 1000 lbs/hr		Cooling Water	
		Norm.	Max.	KW	50 psig / 298 F	Return Cond. 50 Psig / 298 F	Make-up	CW, MMbtu/hr	C.W. circ. GPM
C-301	Acid Gas Absorber						21.5		
E-301A/B	Lean Amine Cooler							36.8	3,674
E-303 A/B	Stripper Condenser							63.3	6,322
E-304	Stripper Reboiler				119.3	(119.3)			
G-301 A/B	Lean Amine Pump	574.1		475.9					
G-302 A/B	Reflux Pump	7.0		6.0					
G-303 A/B	Makeup Water Pump	18.3		14.9					
G-304	Amine Sump Pump (Note 2)	0.8		0.7					
G-305 A/B	DMDA Injection Pump	0.04		0.03					
	TOTAL	600		497	119.3	(119.3)	21.5	100.1	9,996
NOTES: (1) Negative numbers (xxx) are productions while positive numbers are consumptions. (2) Numbers shown are intermittent consumptions and are NOT included in NORMAL total.									

Table B-2 Case 2 - Equipment List

Columns	Item Name	Quantity	Type	Dimensions		Design		Mat'l of Construction (M.O.C)		Comments
				I.D (FT)	T-T (FT)	Press. (PSIG)	Temp (°F)	Shell	Internals	
C-301	Acid Gas Absorber	1	Vertical	10.0	39.5	450	220	CS & SR		SR - Stress Relief
	Valve Trays	12	Internal Devices	10.0	N/A				304 SS	
	Liquid Distributors	2	Internal Devices	10.0	N/A				304 SS	
	Demister Pads	1	Internal Devices	10.0	N/A				304 SS	
C-302	Acid Gas Stripper	1	Vertical	10.5	65.5	50	310	CS/304 SS Clad		
	Valve Trays	20	Internal Devices	10.5	N/A				304 SS	
	Chimney Trays	1	Internal Devices	10.5	N/A				304 SS	
	Liquid Distributors	2	Internal Devices	10.5	N/A				304 SS	
	Demister Pads	1	Internal Devices	10.5	N/A				304 SS	
Vessels & Tanks	Item Name	Quantity	Type	Dimensions		Design		M.O.C	Internals	Comments
				I.D (FT)	T-T (FT)	Press. (PSIG)	Temp (°F)			
D-301	Treated Gas Knockout Drum	1	Vertical	7.0	8.0	440	180	CS	Demister pad	
D-302	Flash Drum	1	Horizontal	9.0	19.0	50	210	CS & SR		
	Flash Drum Top Column	1	Vertical	3.0	6.0	50	210	CS & SR	Demister pad	
D-303	Reflux Drum	1	Vertical	5.5	10.0	20	170	CS & SR	Demister pad	
T-301	MDEA Surge Tank	1	Cone Roof	14.0	45.0	ATM	310	CS		
T-302	MDEA Sump	1	In Ground					Concrete		Capacity: 1700 gal
Exchangers	Item Name	Quantity	Type	Total Duty	Tot. Bare Tube Area	Design		M.O.C		
				MMBTU/HR	SQ FT	Press. (PSIG)	Temp (°F)			
						S	80	240	CS & SR	
E-301A/B	Lean Amine Cooler	2	S & T	36.8	7,290	T	480	240	CS & SR	
						S	30	310	304 SS	
E-302 A/B	Lean/Rich Exchangers	2	S & T	44.8	26,500	T	50	310	304 SS	
						S	30	280	304 SS	
E-303 A/B	Stripper Condenser	2	S & T	63.3	9,100	T	80	280	304 SS	
						S	30	350	304 SS	
E-304	Stripper Reboiler	1	Kettle	109.9	15,325	T	70	350	304 SS	
Pumps	Item Name	Quantity	Type	Design Capacity			Driver		M.O.C	
				Flow (GPM)	Inlet PSIG	Delta PSI	Pump BHP	HP	Casing	Impeller
G-301 A/B	Lean Amine Pump	2	Cent	1,535	2.60	433	574	638	CS	316 SS 2x100%
G-302 A/B	Reflux Pump	2	Cent	138	5.60	14	7	8	CS	316 SS 2x100%
G-303 A/B	Makeup Water Pump	2	Cent	49	ATM	435	18	20	CS	CS 2x100%
G-304	Amine Sump Pump	1	Vert. Cent	29	ATM	10	1	1	CS	CS 1x100%. No Spare.
G-305 A/B	DMDA Injection Pump	2	Meter	0.05	43	942	0.04	0.04	CS	CS 2x100%
Miscellaneous	Item Name	Quantity		Design Capacity		Design		M.O.C		
						Press. (PSIG)	Temp (°F)			
Y-301	Filters (Carbon + Pre & Post Filters)	1	Package	140	GPM of lean MDEA	50	310	CS & SR		5 micron pre & post filters.

Table B-3 Case 2 - Equipment Cost Estimates

DESCRIPTION	QTY	UNIT	COSTS IN US\$ (2Q09)				
			EQUIPMENT	BULK	LABOR	SUBCONTR/ OTHER	TOTAL
<u>PROCESS EQUIPMENT & DUCTWORK</u>							
PUMPS & DRIVERS	10	EA	476,600		36,000		512,600
HEAT EXCHANGERS	7	EA	1,778,400		23,000		1,801,400
TANKS & STORAGE FACILITIES	1	EA	48,533		2,000		50,533
MATL HANDLING & PROCESSING - FILTERS	1	EA	136,500		5,000		141,500
COLUMNS & VESSELS (INCL HEAVY/OVERSIZE TRANSPORT)	5	EA	996,590		36,500		1,033,090
FREIGHT (EQUIPMENT EXCEPT HEAVY/OVERSIZE TRANSPORT)	5	%	<u>171,800</u>				<u>171,800</u>
TOTAL PROCESS EQUIPMENT & DUCTWORK	24	EA	3,608,423		102,500		3,710,923
INSTRUMENTS				541,300	211,000		752,300
PIPING				1,082,500	1,196,000		2,278,500
STEELWORK				216,500	155,000		371,500
INSULATION						360,800	360,800
ELECTRICAL				541,300	668,500		1,209,800
CONCRETE				180,400	258,000		438,400
BUILDING							
SITWORK				180,400	375,000		555,400
PAINTING						36,100	36,100
TOTAL DIRECT COSTS				2,742,400	2,863,500	396,900	6,002,800
TOTAL INSTALLED EQUIPMENT COSTS			3,608,423	2,742,400	2,966,000	396,900	9,713,723

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14. ABSTRACT (Maximum 200 Words) The first section (Task 1) of this report by Nexant includes a survey and screening of various acid gas removal processes in order to evaluate their capability to meet the specific design requirements for thermochemical ethanol synthesis in NREL's thermochemical ethanol design report (Phillips et al. 2007, NREL/TP-510-41168). MDEA and selexol were short-listed as the most promising acid-gas removal agents based on work described in Task 1. The second report section (Task 2) describes a detailed design of an MDEA (methyl diethanol amine) based acid gas removal system for removing CO2 and H2S from biomass-derived syngas. Only MDEA was chosen for detailed study because of the available resources.						
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